

Supreme Court, U.S.  
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82-1090

No.

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IN THE  
**SUPREME COURT OF THE UNITED STATES**  
**OCTOBER TERM, 1982**

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ASHLAND OIL, INC.,

Petitioner,

Vs.

DELTA OIL PRODUCTS CORPORATION,

Respondent.

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APPENDIX IN SUPPORT OF  
PETITION FOR A WRIT OF CERTIORARI TO THE  
UNITED STATES COURT OF APPEALS FOR THE  
SEVENTH CIRCUIT

INDEX TO APPENDIX

<u>JOINT APPENDIX PAGE NO.</u>		<u>PETITION PAGE NO.</u>
A 01-A 06	Seventh Circuit Court of Appeals Decision	1
97	Joint Final Pretrial Report (p.4)	7, 9
98	Joint Final Pretrial Report (p.5)	11
99	Joint Final Pretrial Report (p.6)	10
100	Joint Final Pretrial Report (p.7)	14
211	U.S.D.C. Decision and Order (8/21/80)	2
214-245	U.S.D.C. Decision and Order (3/26/81)	1
246	U.S.D.C. Judgment (4/24/81)	1
247	U.S.D.C. Amended Judgment (5/7/81)	1
215	Decision and Order (3/26/81 - p.2)	7
238	Decision and Order (3/26/81 - p.25)	11
244	Decision and Order (3/26/81 - p.31)	26
295-96	Dr. Robert J. Schafer's Testimony	8
297-9	Dr. Robert J. Schafer's Testimony	2, 3
300	Dr. Robert J. Schafer's Testimony	3
302	Dr. Robert J. Schafer's Testimony	5
304	Dr. Robert J. Schafer's Testimony	5
305	Dr. Robert J. Schafer's Testimony	5
306	Dr. Robert J. Schafer's Testimony	4, 5
310	Dr. Robert J. Schafer's Testimony	6
316-18	Dr. Robert J. Schafer's Testimony	9
320-21	Dr. Robert J. Schafer's Testimony	9
321	Dr. Robert J. Schafer's Testimony	10

<u>JOINT APPENDIX</u>		<u>PETITION</u>
<u>PAGE NO.</u>		<u>PAGE NO.</u>
382	Anton Dorfmüller's Testimony	7
383-7	Anton Dorfmüller's Testimony	8
388	Anton Dorfmüller's Testimony	10
394	Anton Dorfmüller's Testimony	14
398	James W. Sparks' Testimony	2
406-9	James W. Sparks' Testimony	11
429	James W. Sparks' Testimony	11, 12
429-30	James W. Sparks' Testimony	14
443	James W. Cartwright's Testimony	12
449-54	James W. Cartwright's Testimony	13
459	James W. Cartwright's Testimony	14
461	Leo J. LeBlanc's Testimony	13
464-9	Leo J. LeBlanc's Testimony	13
467-8	Leo J. LeBlanc's Testimony	14
1198-1204	Isocure Patent 3,409,579	2
1205-1210	Pep Set Patent 3,676,392	2
1760	C E Cast License	14
1866-67	Graph - Consumption of Major Sand Binders	12

In the

# United States Court of Appeals

For the Seventh Circuit

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No. 81-1895

ASHLAND OIL, INC.,

*Plaintiff-Appellant,*

v.

DELTA OIL PRODUCTS CORPORATION.

*Defendant-Appellee.*

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Appeal from the United States District Court  
for the Eastern District of Wisconsin.  
No. 76 C 131—Terence T. Evans, Judge.

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ARGUED DECEMBER 9, 1981—DECIDED JUNE 7, 1982\*

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Before SPRECHER,\*\* BAUER, Circuit Judges, and Roszkowski, District Judge.\*\*\*

PER CURIAM. Before the court is an appeal from the decision of the United States District Court for the

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\* This appeal was originally decided by an unpublished order on June 7, 1982 pursuant to Circuit Rule 35. The court has subsequently decided to issue that decision as an opinion.  
\*\* Judge Sprecher read the briefs, heard the oral arguments, and participated in the conference thereafter, but passed away before the decision was prepared.

\*\*\* The Honorable Stanley J. Roszkowski, Judge of the United States District Court for the Northern District of Illinois, Eastern Division, is sitting by designation.

Eastern District of Wisconsin which invalidated two of the plaintiff's United States Letter Patents. With one exception, this court adopts the memorandum opinion of the district court in its entirety. The decision below is therefore affirmed in part and reversed in part.

The plaintiff, Ashland Oil, manufactures and sells chemical products to foundries through its Chemical Division. The defendant, Delta Resins & Refractories, formerly known as Delta Oil Products Corporation, also manufactures and sells foundry products. The parties dispute centers upon their respective chemical binders which, when mixed with sand, form a mold into which molten steel is poured to form a casting. The plaintiff alleged, at trial, that Delta's "Quick Set" chemical binder and "Cold Box" process infringes Ashland's United States Letter Patent No. 3,409,579 ('579 patent) issued on November 5, 1968 and Ashland's United States Letter Patent No. 3,676,392 ('392 patent) issued on July 11, 1972. The trial court below held that Ashland's patents were invalid and therefore unenforceable against the defendant. The pertinent facts are as follows.

In the foundry industry, chemical compositions called "chemical binders" are mixed with sand. The resulting mixture is then compacted around a pattern, and then removed from the pattern. The form or shape removed is a mold into which molten steel is poured. After the molten steel solidifies, the sand mold must break down to permit the sand to be shaken out of the casting. Finished foundry castings can be seen as door handles, cylinder bores in automobile engines, and the like.

A desirable chemical binder for the industry would possess the following attributes when mixed with sand: quick curing, curable without heat, able to provide high dimensional tolerances, strength sufficient to avoid deforming when molten steel is poured into it, and a break down time which occurs quickly after, and only after, the casting has solidified.

As the trial court's opinion explains in detail, five binder processes were generally used in the industry

prior to the early 1960's. Each had its advantages and disadvantages. No one process was able to incorporate all the features the foundry industry desired.

In 1965, the Archer Daniels Midland Company, predecessor to Ashland's Chemical Division, hired Dr. Janis Robins to develop a binder system that would cure quickly at room temperature. The research that began in 1965 eventually led to three patents.

Dr. Robins early work led to the discovery of the polybenzylic ether resin which became known as the "pep resin." The pep resin was the subject of Ashland's first patent, U.S. Patent No. 3,485,797 (the '797 patent). The '797 patent was not at issue in this suit.

In the latter part of 1965, Dr. Robins invented a binder process called the "Isocure" process. The Isocure invention was later patented in 1968 under U.S. Patent No. 3,409,579 (the '579 patent).

The Isocure process became a huge commercial success. Plaintiff Ashland Oil's annual worldwide sales of Isocure ran approximately sixty million pounds by 1979. Isocure's success was due to its quick set, ability to cure without heat, and the hard smooth core surfaces it produced.

After discovering the Isocure binder system, Dr. Robins continued his work and developed what has become known in the trade as the Pep Set. The Pep Set invention was patented in 1972 under U.S. Patent No. 3,676,392 (the '392 patent). The Pep Set binder system includes a curing agent, a polyisocyanate, and a soluble resole resin or a Pep Resin. The Pep Set binder system, which also cures without heat, has a primary advantage of curing almost instantly. Pep Set, like the Isocure process, also became a huge commercial success.

The defendant, Delta Oil, competes in the foundry binder market. In the Fall of 1975, Delta introduced its Quick Set and Cold Box binder systems to compete with Ashland's Pep Set and Isocure, respectively.

On February 23, 1976, Ashland Oil filed this suit against Delta Oil alleging infringement of the Robins

'579 and '392 patents. Specifically, Ashland has accused Delta of infringing Claims 1 and 13 of the '579 patent and Claims 1 and 16 of the '392 patent through Delta's manufacture and sale of its "Quick Set" foundry binder system. Ashland also accused Delta of infringing Claims 1, 13, 15, 16 and 18 of the '579 patent through its manufacture and sale of its Delta "Cold Box" process.

Delta affirmatively defended by alleging that Ashland's patent claims were invalid for obviousness under 35 U.S.C. § 103. In addition, Delta claimed that the '392 patent was invalid for double patenting.

The district court conducted an eight day bench trial from October 29, 1980 through November 7, 1980. The Court entered its decision and order on March 26, 1981. The Court held all of the patent claims were invalid for obviousness and that all of the claims of the '392 patent were invalid for double patenting.

Ashland now appeals from that decision. Although Ashland presents numerous grounds for appeal, Ashland's primary emphasis is on three arguments.

First, Ashland argues that the district court erred when it failed to consider the huge commercial success of plaintiff's inventions when it held that the inventions were obvious under 35 U.S.C. § 103.<sup>1</sup> The United States Supreme Court, in *Graham v. John Deere*, 383 U.S. 1, 17-18, 86 S.Ct. 684, 15 L.Ed.2d 545 (1966), set forth the three major factors to be addressed when resolving a § 103 claim of obviousness.

Under § 103, the scope and content of the prior art are to be determined; differences between the prior art and the claims at issue are to be ascertained;

<sup>1</sup> A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. 35 U.S.C. § 103.

and the level of ordinary skill in the pertinent art resolved. Against this background, the obviousness or nonobviousness of the subject matter is determined.

The Court also held that other secondary factors may also be considered.

Such secondary considerations as commercial success, long felt but unsolved needs, failure of others, etc., might be utilized to give light to the circumstances surrounding the origin of the subject matter sought to be patented. As indicia of obviousness or nonobviousness, these inquiries may have relevancy.

*Id.* (Emphasis supplied).

This Court has held that the secondary considerations in *Graham* may be weighed "[o]nly in a close case, in which application of the primary criteria of nonobviousness under section 103 does not produce a firm conclusion." *Republic Industries, Inc. v. Schlage Lock Co.*, 592 F.2d 963, 975-76 (7th Cir. 1979) (emphasis supplied).

In the present case, the district court held that "the 'primary criteria of obviousness' warrant a finding of obviousness" and stated further that the court does "not believe this a close enough case to warrant the weighing of secondary considerations." (Memorandum Opinion at 16-17). The district court's refusal to consider or weigh secondary considerations was therefore a proper application of our holding in *Republic Industries, supra*, and we find no error.

Second, Ashland contends the district court erred when it gave greater weight to the testimony of Delta's expert, Dr. Wendland, than it gave to Ashland's experts Drs. Frisch and Schafer. Ashland claims that Dr. Wendland was not an expert in polyurethane chemistry and had no foundry experience. On the other hand, Drs. Schafer and Frisch were experts in both areas and both testified that the inventions were unobvious.

This court finds no error in the district court's reliance on Dr. Wendland. He has his doctorate in chemis-

try, taught the subject at the collegiate level for over fifteen years, and has authored over a dozen technical publications in the area. Moreover, Ashland did not object at trial to Dr. Wendland's qualifications as an expert. The court was therefore well within its discretion to consider and rely upon the testimony of Dr. Wendland.

Third, Ashland contends the district court erred when it invalidated all 17 claims of the '392 patent for double patenting. This court agrees. A review of the record shows that only claims 1 and 16 of the '392 patent were placed in issue before the District Court. This Circuit, as well as others, have held that it is error to invalidate all of a patent's claims when only a number of the patent's claims are actually litigated before the court. See *Laufenberg, Inc. v. Goldblatt Bros.*, 179 F.2d 832 (7th Cir. 1950); *Palmer v. Orthokinetics, Inc.*, 611 F.2d 316 (9th Cir. 1980); *Westwood Chemical Inc. v. Owens-Corning Fiberglass Corp.*, 445 F.2d 911 (6th Cir. 1971), cert. denied, 405 U.S. 917 (1972). Accordingly, the portion of the district court's opinion invalidating claims 2-15 and 17 of the '392 patent is hereby reversed.

This court has reviewed the various other grounds raised by the Appellant and finds them to be without merit.

The district court is therefore affirmed in part and reversed in part.

A true Copy:

Teste:

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*Clerk of the United States Court of Appeals for the Seventh Circuit*

FILED UNDER THE PROTECTIVE ORDER

IN THE UNITED STATES DISTRICT COURT  
FOR THE EASTERN DISTRICT OF WISCONSIN

ASHLAND OIL, INC.,      )  
                        )  
Plaintiff,              )  
                        )  
vs.                      ) Civil Action No. 76-C-131  
                        )  
DELTA OIL PRODUCTS      )  
CORPORATION,            )  
                        )  
Defendant.              )

JOINT FINAL PRETRIAL REPORT

I. Agreed Statement of all Uncontested Facts

The Parties and Jurisdiction

1. Ashland Oil, Inc., a corporation of the Commonwealth of Kentucky, transacts business within this district. Its division, Ashland Chemical Company, sells foundry products in this Commonwealth.

2. Delta Oil Products Corporation, which has legally changed its name to Delta Resins & Refractories, is a corporation of Wisconsin having its principal place of business in Milwaukee. Delta's principal business comprises the sale of chemical products to the foundry trade, the major amount thereof being products for use in the foundry industry. The products accused by Ashland to infringe its patents comprise a minor amount of the gross sales volume of Delta.

3. The parties agree that jurisdiction and venue are proper in this Court by virtue of 28 U.S.C. §1338 and §1400(b).

The Patents in Suit

4. Ashland is and has been, at all times relevant hereto, the owner of the two patents in suit, to wit: 3,409,579 ('579) and 3,676,392 ('392). Ashland accuses Delta of infringing Claim 13 of the '579 patent and Claim 16 of the '392 patent by reason of Delta's manufacture, use and sale of a foundry binder system called Quick Set. Ashland also accuses Delta of infringing Claims 13, 15, 16 and 18 of the '579 patent by Delta's manufacture, use and sale of a product called Delta Cold Box (880-X).

5. One feature of Pep Set®, a no-bake binder manufactured by Ashland under the two patents in suit, is that after it is mixed with sand, the sand can be worked or mixed without any apparent cure. Thereafter, the binder cures rapidly and in a short time the sand core or mold may be removed from the pattern and used.

Background and Development of the Inventions of the Patents in Suit

6. In the art of foundry practice, a metal casting is formed by pouring molten metal into a mold, usually formed by sand which has first been compacted around a pattern and the pattern thereafter removed to form a cavity into which the molten metal is poured.

7. The mold often includes cores which have been formed by sand and a binder, with the binder having been cured so that the core remains firm and intact during the metal pouring process until the surface of the metal solidifies sufficiently. The cores are used to form the internal configuration of the casting such as the cylinder bores in an automobile engine. After the metal has solidified, the binder must break down sufficiently to permit the sand to be shaken out of the casting.

8. A number of binders were in use in the 50's and early 60's and many of them are in use today. Among the major suppliers of core binders in the early 60's were Aristo-IMC, Acme, DuPont, Hooker, Borden, Delta and Reichhold Chemical Co. Archer Daniels Midland Company, which was the predecessor to the plaintiff company, the Chemical Division of Ashland Oil, Inc., was a supplier of binders.

9. In the early 1960's, most cores were formed by curing the binders in one of five principal processes:

(a) Oven cured binders (such as core oils) were mixed with sand and a green strength-producing agent (producing some strength in an uncured state) and formed to the desired shape in a core box. The cores were removed from the core box and conveyed to an oven where they were baked over a period of time to complete the cure.

(b) In the hot box process, a heat setting binder and catalyst, was mixed with sand and formed in a core box to the desired shape. Heat was directed onto the core box, as by a direct flame, to effect the cure of the binder.

(c) In the CO<sub>2</sub> silicate process, the silicate binder was mixed with sand, placed in a core box and CO<sub>2</sub> gas was blown through the core to effect the cure.

(d) In the no-bake process, the sand was mixed with chemicals and placed in the core box. There, through a chemical reaction, and without the application of heat, the binder cured to form the core. Furans, silicates and alkyd resins were among the no-bake resins.

(e) The shell process was similar to the hot box process in that a heat-curable binder was employed but only a shell a fraction of an inch thick was formed in the core box with the excess uncured sand being poured out of the core before

curing, the binder cured by the contact of the sand with which it was mixed against the hot surface of the tooling in the core box. Each party to this action sold various of the binders referred to above.

10. The different types of binders had advantages and disadvantages with respect to one another. Among the disadvantages which appear in one or another of the binders of paragraph 9 were the slowness of the cure; the lack of precision in the surface configuration of the core; the heat energy required to cure the core; the inability to shake the cores out of the casting; poor shelf life for the binder; poor shelf life for the core; a high percentage of core scrap; and a high percentage of casting scrap.

11. In the 50's and early 60's, there were widespread attempts to improve upon the quality of the binders. For example, DuPont introduced a sodium silicate binder, but it was too hard to shake out of the casting and never had any significant impact in the marketplace.

12. Dr. Schafer, an ADM employee, jointly invented a no-bake binder described in Patent No. 3,255,500, which has been successfully marketed by Ashland under the trademark Linocure®. Ashland has granted licenses under the patent to other binder manufacturing companies, including Delta.

13. In 1965, ADM hired Dr. Janis Robins who had considerable expertise in phenolic and urethane chemistry but no substantial foundry experience. Dr. Robins was given a relatively free rein to experiment, and in the course of his work discovered the polybenzylidene ether resin of Ashland's U. S. Patent 3,485,797, not in suit.

14. Isocure® was introduced into the market in 1968 and has over the years achieved commercial success. The Isocure® binder system has been adopted by a great many of the major foundries in the United States and the rest of the world. Additionally, the Isocure® binder has resulted in the development and marketing of new gassing apparatus and scrubbing apparatus.

15. Whereas the Isocure® cold box process involved the steps of admixing the resin and the polyisocyanate with sand, the blowing of that mixture into the core box and the subsequent gassing of the mixture with the amine catalyst in order to effect a cure, the Pep Set® no-bake process involved the forming of an admixture of the resin and the polyisocyanate hardener and the catalyst mixed with the sand before introduction into the core box. After introduction into the core box, the chemicals reacted with one another to cure the binder around the grains of sand to form the core without any external application of heat or further catalyst.

16. For some period of time prior to the April 1970 introduction of Pep Set®, it and its predecessors (products called "Isocure no-bake" and EP 54-51) were tested in several different foundries. Some of these tests were carried out prior to January 26, 1970.

17. After its introduction, Pep Set® became a commercial success in the United States and the rest of the world.

18. Ashland contends and Delta does not contest that plaintiff's Isocure® product is made, and has always been made, using a benzylic ether phenolic resin as described and claimed in U. S. Patent 3,485,797 as the phenolic resin. When mixed with sand and cured with a gaseous amine, plaintiff's

product and its use is within the scope of Claims 13, 15, 16 and 18 of the '579 patent.

19. As commercially practiced, plaintiff's Isocure® product is, and has always been, within the scope of Claim 6 of the '579 patent as well as other claims.

20. Ashland contends and Delta does not contest that plaintiff's Pep Set® product is made, and has always been made, using a benzylic ether phenolic resin as described and claimed in U. S. Patent 3,485,797 as the phenolic resin. When mixed with sand, plaintiff's product is within the scope of Claim 16 of the '392 patent and Claim 13 of the '579 patent.

21. Plaintiff's commercial Pep Set® product is within, and has always been within, the scope of Claim 6 of the '579 patent and Claim 7 of the '392 patent as well as other claims.

22. The first filed patent application directed to plaintiff's Isocure®, or its predecessor in name, was filed August 1, 1966. Isocure® was not introduced commercially until 1968.

23. For the purpose of this suit, the first patent application filed by Robins directed to plaintiff's Pep Set®, or its predecessor in name, was filed April 24, 1968. Pep Set® was not introduced commercially until 1970. Field testing of plaintiff's Pep Set®, or its predecessor in name, took place in the latter part of 1969.

Long-Felt Need--Failure of Others

24. Pep Set® has achieved a substantial success in the marketplace with millions of pounds being sold annually. It has certain qualities such as tensile strength, work time, and strip time that other competitors, including Delta, have sought

to equal.

(a) Two of Ashland's major competitors, International Minerals and Chemical Co. and Combustion Engineering (C E Cast Division) have taken licenses under the '392 patent as well as licenses under the '579 and '797 patents.

(b) Ashland has offered Delta a license under the patents in suit and it was rejected.

25. Prior to its introduction of Quick Set, Delta was in the business of supplying products, including binders, to foundries. In 1974, Delta surveyed the foundry binder market for the purpose of determining what products then being sold afforded the most likely prospect for the easiest market penetration. Delta observed that the Pep Set<sup>®</sup> binder system market (phenolic urethane) had the prospects for quickest market penetration.

26. Quick Set was developed and offered for sale in the fall of 1975 to compete with Pep Set<sup>®</sup>. Delta's cold box product was also offered for sale in the fall of 1975. At that time Delta had knowledge of the patents in suit but had not received any validity or infringement opinion with respect thereto.

27. The accused Delta binder system which Ashland alleges infringes Claim 13 of the '579 patent and Claim 16 of the '392 patent is called Quick Set. Quick Set has been and is sold as a three part system for use as a foundry sand binder. Ashland does not contend that Quick Set infringes the claims of the patents in suit which are specifically and solely directed to the use of benzylic ether phenolic resins.

28. The accused Delta Quick Set system is a three part system. One part of the system (called by Delta 580-X or

590-X) has always included a polyether polyol and one of three phenolic components referred to by Delta as 248 Resin, 629 Resin and 645 Resin and sometimes included a novolac resin.

Delta's first Quick Set product included one part called 580-X comprising a phenolic material designated by Delta as 248 Resin, a polyether polyol and a novolac resin. At least some of the 248 Resin sold by Delta in 580-X was a "methylol-terminated phenolic resin which comprises a resole resin which is organic solvent soluble," within the language of Claim 16 of the '392 patent. Thereafter, in November 1976, Delta replaced the 248 Resin in 580-X with 629 Resin. The manufacturing instructions for 629 Resin specified 8 to 10% water. When Delta acquired its resin manufacturing facility in the Spring of 1978, several experimental batches of 629 were made wherein the water content was reduced to less than 5%. The "low water" 629 was then designated 645 Resin.

29. One part of the Delta Quick Set system has always been a "co-reactant" which has contained a polyisocyanate in solvent. The co-reactant has been code numbered 630-X or 635-X. The Delta polyisocyanate corresponds to the liquid polyisocyanate containing at least two isocyanate groups of Claim 13 of the '579 patent and Claim 16 of the '392 patent.

30. Another part of the Quick Set system has always been an "activator" part. The "activator" part has always contained an organic tin catalyst and an alkyl-substituted pyridine catalyst. The alkyl-substituted pyridine is a tertiary amine curing agent as defined in Claim 13 of the '579 patent and is a base having a  $pK_b$  value in the range of about 7 to about 11 as defined in Claim 16 of the '392 patent. Ashland contends and Delta does not contest that the inclusion of the organic tin compound in Delta's activator does not obviate infringement of 101

either patent.

31. Delta admits that at least some of the 248 Resin was a resole phenolic resin. Delta admits that the three part Quick Set system, which included such 248 Resin in the 580-X, was combined with the co-reactant part and the activator part and was used by a foundry and was an infringement of Claim 16 of the '392 patent. (If held valid and construed in accordance with Ashland's contention, infra). Ashland contends, and Delta does not contest, the addition of the polyol and/or novolac to the 580-X and the addition of the tin compound to the activator do not obviate infringement.

32. The procedure which Delta specified for making 248 Resin that was used from the Fall of 1975 to about November 1976, with changes as noted below, was as follows:

248 Low Water Phenolic Resin Procedure

Formula:

Phenol - USP	57.6%
Formalin 52% uninhibited	42.4%

Additions:

25% NaOH	2.0%
30% Toluene Sulfonic Acid	5.0%

Procedure:

1. Add phenol, formalin, and NaOH to reaction type kettle (sketch of this type kettle is included.)
2. Keep temperature at 70°C (Exothermic reaction of phenol and formalin will bring mixture to this temperature) for 1½ hours.
3. At this point, free formaldehyde determined by the sodium sulfite method should be less than 1%.
4. Slowly add the 30% TSA to bring the PH to 4.3-4.7.
5. Hold temperature at 70°C and vacuum strip to 3.8 to 4.2.
6. Adjust PH to 3.5 to 4.

Specs for Resin:

Water content (Carl Fisher) 3.8 to 4.2 per cent  
PH - 3.5 to 4.0.  
Viscosity 2000 to 2400 CPS (70°F)

This procedure was adapted from a standard reference chemistry book. Plaintiff's Deposition Exhibit 13 is a modified procedure also specified.

33. Plaintiff's Deposition Exhibit 28 shows the quantity of 248 Resin received by Delta, its water content and viscosity.

Delta 629 Resin

34. In about November 1976, Delta changed the procedure specified for making 248 Resin so as to obtain 629 Resin. The manufacturing procedure specified by Delta for 629 Resin was as follows:

629 Phenolic Resin Procedure

CONFIDENTIAL

Formula:

Phenol USP	57.6%
Formalin 52% uninhibited	42.4%

Additions:

25% NaOH	2.0%
30% Toluene Sulfonic Acid	5.0%

Procedure:

- 1) Add phenol, formalin, and NaOH to reaction type kettle.
- 2) Keep temperature at 70°C (Exothermic reaction of phenol and formalin will bring mixture to this temperature) for 1½ hours. -4 AMZ.
- 3) At this point, free formaldehyde determined by the Hydroxylamine HCl method should be .8% -.9%.
- 4) Slowly add the 30% TSA to bring the pH to 4.3- 4.7.
- 5) Hold temperature at 70°C and vacuum strip to 8- 10% water.  
- 75°C

Specs for Resin:

- 1) Water content (Carl Fisher) 8 to 10 percent.
- 2) pH 4.3 to 4.5.
- 3) Viscosity 200 to 350 CPS 77°F.

35. Plaintiff's Deposition Exhibits 29 and 89 are Delta's Quality Control Cards for 629 Resin. As noted on the cards, all of 629 Resin manufactured by Georgia Pacific contained more than 5% by weight water. In 1978 three batches of 629 were produced which contained less than 5% by weight water. The low water 629 Resin was renamed 645 Resin which is regularly made with less than 5% water. 629 Resin with a specified water level of 8 to 10% is still produced regularly by Delta as is shown by plaintiff's Deposition Exhibit 89.

36. Most of 248 Resin and some 629 Resin used by Delta was purchased from Georgia Pacific. Georgia Pacific's code numbers were GP-2199 and GPX 15-15, respectively.

Delta 645 Resin

37. Delta's first procedure for manufacturing 645 Resin is typified by the appropriate batch sheet in plaintiff's Deposition Exhibit 105.

38. Delta's procedure for making 645 Resin that has been used since the summer of 1979 is as follows:

Tentative Commercial Production of Raw Material 645

(Basis 10,000 lb. charged)

- 1) Charge kettle with 6,470 lb. phenol (99+%), 710 lb. water, 2,500 lb. paraformaldehyde with stirring.
- 2) Heat to 50°C. and hold.
- 3) Add a mixture of 58 lb. KOH in 52 lb. water to kettle.
- 4) Check pH.
- 5) If pH is less than 8.7, add mixture of  $\frac{1}{2}$  lb. KOH in  $\frac{1}{2}$  lb. H<sub>2</sub>O to kettle. Stir 5 mins.; go to step (4). If pH is 8.7 - 9.2, set vacuum to 17". If pH is greater than 9.2, add 2 lb. TGA; go to step (4).
- 6) Heat at rate of 1°C./min. to 85°C., and hold at 85°C. for 1 hr. 45 mins. Hold vacuum at 17" throughout.
- 7) Sample and run free formaldehyde (FF).

- 8) If FF less than 1.8 to 1.9, cool kettle to 75°C. If FF greater than 1.8 to 1.9, re-engage and maintain vacuum. Continue heating (see foreman for length of time) at 85°C. and then go to step (7).
- 9) Add 200 lb. TSA; wait 5 mins.
- 10) Check pH.
- 11) If pH is greater than 5.9, add 10 lb. TSA; wait 5 mins.; go to step (10). If pH is equal to 4.9 - 5.5, apply full vacuum and 100% heat to kettle. If pH is less than 4.9, add ½ lb. KOH in ½ lb. water; go to step (10).
- 12) Continue strip until 42° condensate are observed.
- 13) Turn off heat and vacuum.
- 14) Take samples for water, FF, and turbidity analysis. Re-engage vacuum.
- 15) Run Karl Fischer water analysis at once; determine FF and turbidity later.
- 16) If water greater than 2%, maintain full heat and vacuum on kettle (see foreman for length of time). Repeat steps (14) and (15), except for FF sample and analysis. If water less than 2%, cut vacuum and increase kettle temp. to 95°C. Hold for 1 hr.
- 17) Sample for turbidity analysis, and determine turbidity.
- 18) If turbidity is 20-25 ml., cool to 45°C. and package product. If turbidity is greater than 25 ml., hold kettle at 95°C. (see foreman for length of time). Repeat step (17).

NOTES:

- A) Because of steps (8), (16), and (18), it is necessary that foreman be present for all runs. If procedure is removed from tentative status and finalized after operators are trained, this requirement may be dropped.
- B) Packaging may involve addition of BCA on occasion. In this event, Milwaukee Manager of Mfr. Operations must be notified in detail to this effect at once.
- C) If BCA is not added, the material must meet specs. of 645 raw material, or labelled as rework. In this case Milwaukee Manager of Mfr. Operations must be notified to this effect before any shipment from Chicago to Milwaukee.

Plaintiff's Deposition Exhibit 105 contains the actual batch log sheets showing the conditions employed.

Use of Delta's Quick Set Binder System

39. See attached stipulation appended hereto. The Quick Set referred to in said stipulation embraces 248 Resin, 629 Resin and 645 Resin.

Use of Quick Set

40. Delta sells its Quick Set for making foundry cores and molds. Ashland sells its Pep Set® for making foundry cores and mold.

Delta's Cold Box System

41. Prior to April 1976, Delta offered for sale a cold box binder system. This binder system was demonstrated to foundries and it was used by said foundries in their commercial equipment to manufacture molds and/or cores which were used to produce castings.

42. As demonstrated in said foundries, the Delta cold box binder system comprised an 880-X part containing a polyether polyol, a novolac, and 248 Resin and a "co-reactant" part comprising a polyisocyanate. A gaseous tertiary amine was used as a curing catalyst.

The court is not willing at this stage to hold that the resin components are so unrelated that the commercial success of the marketed products would not tend to support the claimed unobviousness of the Isocure and Pep Set claims in suit.

Exclusion of the evidence now for the reasons proposed by Delta Oil would be tantamount to adoption of a per se rule; commercial success evidence of a product species not in suit can never be admitted to support the patentability of claims in suit. The court is not willing to go that far in light of the broad definition of relevant evidence in Rule 401 F.R.C.P.

This is a trial to the court, not a jury trial. When the issue arises at trial, the court will best be able to determine the relevance of this evidence. The court is not now willing, or able, to conclude that the Claims in suit are so unrelated to those not in suit that the commercial success of one product has no bearing on the other. The relevance may in fact be marginal, but the court at this stage is not prepared to exclude this evidence from the trial.

IT IS THEREFORE ORDERED THAT:

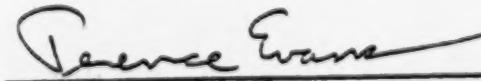
Defendant's motion to exclude from suit Claims 15, 16 and 18 of patent '579 is denied.

Defendant's motion to include in suit Claim 1 of each patent is granted.

Defendant's motion to exclude plaintiff's evidence of "commercial success" of products not in suit is denied.

Dated at Milwaukee, Wisconsin, this 21 day of August, 1980.

BY THE COURT:

  
TERENCE T. EVANS  
UNITED STATES DISTRICT JUDGE

U.S. DISTRICT COURT - MILWAUKEE, WISCONSIN  
FILED

MAR 26 1981

UNITED STATES DISTRICT COURT at \_\_\_\_\_ o'clock M  
EASTERN DISTRICT OF WISCONSIN RUTH W. LA SALLE, CLERK

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ASHLAND OIL, INC..

Plaintiff,

v.

Civil Action  
No. 76-C-131

DELTA OIL PRODUCTS  
CORPORATION,

Defendant.

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DECISION and ORDER

The patent infringement/validity claims of this five-year-old lawsuit were tried to the court for eight days in November of 1980. The case was extremely well presented by lead counsel for the parties: Bruce Tittel of Cincinnati, Ohio for the plaintiff Ashland Oil, Inc., and Donald Egan of Chicago, Illinois for the defendant Delta Oil Products Corporation. At the conclusion of the trial I took the case under advisement--stating that a decision would be written after studying post-trial arguments.

Ashland Oil manufactures and sells chemical products to foundries through its Chemical Division. Delta Resins & Refractories, formerly known as Delta Oil Products Corporation, also manufactures and sells foundry products.

The foundry industry is the fifth largest industry in the United States in terms of value added to products. In foundry practice, sand is first compacted around a pattern and cured with a chemical binder. The pattern is then removed, and molten metal poured into the resulting cavity. The chemical binder insures that the sand core remains firm and intact while the metal is poured and until the metal's surface solidifies. After solidification, the binder must break down to permit the sand to be shaken out of the casting. Foundry castings can be seen as door handles, cylinder bores in automobile engines, and the like.

A number of binder systems used in the 1950s and 1960s are still used today. In the early 1960s, most cores were cured by one of five processes:

(a) Oven-cured binders were mixed with sand and a green strength-producing agent (producing some strength in an uncured state) and formed to the desired shape in a core box. The cores were removed from the box and taken to an oven, where they were baked for a time to complete the cure.

(b) In the "hot box" process, a heat-setting binder and catalyst were mixed with sand and formed in a core box to the desired shape. Heat was directed on the box to cure the binder.

(c) In the CO<sub>2</sub> silicate process, silicate binder was mixed with sand and placed in a core box. CO<sub>2</sub> gas was then blown through the core to cure the binder.

(d) In the "no-bake" process, the sand was mixed with chemicals and placed in the core box. There, through a chemical reaction and without the application of heat, the binder cured to form the core. Furans, silicates and alkyd resins were among the no-bake resins used.

(e) The shell process was similar to the hot box process in its use of a heat-curable binder. However, only a shell less than an inch thick was formed in the core box, with the excess uncured sand poured out of the core before curing. The binder was cured by contact with the sand with which it was mixed against the hot surface of the tooling in the core box.

Both Ashland and Delta sold varieties of the five binders mentioned above. Each binder had advantages and disadvantages. Among the disadvantages in one or another of the

binders were slowness of cure; lack of precision in the core's surface configuration; heat energy required to cure the core; inability to shake the cores out of the castings; poor shelf life of the binder; poor shelf life of the core; a high percentage of core scrap; and a high percentage of casting scrap. The hot processes produced cores lacking dimensional accuracy, and created handling problems for foundry workers as well as noxious gases. Their production rate was low, and they required energy to cure the cores. The no-bake processes had other deficiencies.

In 1965, the Archer Daniels Midland Company, predecessor to Ashland's Chemical Division, hired Dr. Janis Robins to try to develop a binder system that would cure quickly at room temperature. In his work, Dr. Robins discovered the polybenzylic ether resin of Ashland's U.S. Patent No. 3,485,797 (the "'797 patent," not in suit here) (Exhibit 301), which became known as the "pep resin." In Fall, 1965, Dr. Robins invented the "Isocure" process, later patented under U.S. Patent No. 3,409,579 (the "'579 patent," Exhibit 1, the first patent in suit here).

The '579 patent, entitled "Foundry Binder Composition Comprising Benzylic Ether Resin Polyisocyanate and Tertiary Amine," was issued in Dr. Robins' name on November 5, 1968, based on an application filed May 2, 1967. The second patent in suit, U.S. Patent No. 3,676,392 (the "'392 patent") (Exhibit 2), entitled "Resin Compositions," was issued in Dr. Robins' name on July 11, 1972, based on an application filed January 26, 1971. Both patents in suit trace their heritage back to patent application serial No. 536,180 (Exhibit 307), filed in Dr. Robins' name on March 14, 1966. That application became the '797 patent, entitled "Phenolic Resins Containing Benzylic Ether Linkages and Unsubstituted Para Positions," issued on December 23, 1969 in Dr. Robins' name. The '797 patent claims the polybenzylic-ether phenolic resins used in both Ashland's Isocure and Pep Set binder products.

Ashland has accused Delta of infringing Claims 1 and 13 of the '579 patent and Claim 16 of the '392 patent through Delta's manufacture and sale of its "Quick Set" foundry binder system. Delta is also accused of infringing Claims 1, 13, 15, 16 and 18 of the '579 patent through its manufacture and sale of its Delta "Cold Box" (880-X) process.

Trial Exhibits

Both parties have renewed objections to certain trial exhibits in post-trial briefs.

Ashland has objected to exhibits 370-377, 380, 382-398, 400-403, 407-410 and 415. It makes hearsay objections to all except exhibits 382-390, which Ashland considers untrustworthy because the identity of the standards is not known. Delta has responded by quoting the Pretrial Stipulation, which provides, in part:

"1. Each and every document previously produced or made available for production by a party herein where the document was authored by an employee of the party shall, unless proven otherwise, be deemed to be authentic and genuine and to have been written, published, or issued on or about the date shown by the person, persons or organization appearing thereon, and where applicable, that it was received in due course thereafter by the addressee show, if any." (Emphasis added).

All of the exhibits to which Ashland objects, except exhibits 380, 402, 410 and 415, are documents authored by Delta employees. Thus, under the Pretrial Stipulation, they are admitted.

Exhibit 380 is a nuclear magnetic resin (NMR) spectrum run by Delta employee J. Krogh from a sample of "629" phenolic given him by Dr. Russell LaBar, at that time Delta's Research Group Leader. While an NMR spectrum is not, technically speaking, "authored" by one who runs it, such labwork seems similar to the authorship provision of the Pretrial Stipulation and thus is sufficiently trustworthy to be admitted under Rule 803(6) of the Federal Rules of Evidence.

Exhibit 402 is a collection of NMR spectra analyzing Delta's Quick Set, which was produced by Ashland during pretrial discovery. Ashland has not presented evidence to show that its own submission was not trustworthy. Moreover, the exhibit qualifies as an admission by a party opponent under Federal Rule of Evidence 801(d)(2).

Exhibit 410 consists of pages selected from the Glossary of Terms Relating To Rubber And Rubber Technology, published in 1972 by the American Society for Testing and Materials. Dr. Wendland, Delta's expert, testified with regard to Exhibit 410 at trial, and so that exhibit will be admitted for what it's worth over Ashland's hearsay objection. Similarly, Exhibit 415 is an article from the February, 1979, issue of Modern Casting magazine. Jordan Kopac of Delta testified that this article states that in the past 30 years, metal casting has been revolutionized by a number of new techniques. In last position, the article lists the chemical bonding and cold box processes through which Ashland has claimed to revolutionize the foundry industry. Delta offers this article not for the truth of the matters it states, but rather as evidence that neutral, knowledgeable people in the foundry field regard Ashland's Pep Set and Isocure products as less than revolutionary. On that limited basis, Exhibit 410 will be admitted.

Ashland's objection to Exhibits 382-390, which relates to the high-pressure liquid chromatography (HPLC) work done by the chairman of Marquette University's chemistry department, is an effort to renew its motion to strike Dr. Hoffman's testimony. I denied that motion at the close of trial, and will deny the present motion on the same ground: any lack of authenticity of the chemical components used in the HPLC analysis will affect the weight, not the admissibility, of Exhibits 382-390. The chemical components were obtained from a reputable chemical company, Aldrich Chemical.

Delta has objected to Exhibits 169-174 and 195-197. In response, Ashland has withdrawn its offer of Exhibits 172-174. Delta's objections of the internal inconsistency of Exhibits 170 and 171, based on the testimony of Ashland employee James Sparks, seem well taken. The exhibits will be admitted, however, with the inconsistency affecting only the weight, not the admissibility, of that evidence. Delta has not specified its objections to the remaining exhibits in dispute, which relate to the alleged success of Ashland's products and their acceptance by the foundry industry. All of these exhibits were identified and discussed at trial, and will be admitted.

The '579 Patent

Claim 1 of the '579 patent discloses a three-part binder system comprised of an admixture of a phenolic resin, a polyisocyanate (as a hardener), and a tertiary amine (as a curing agent). Claim 1 defines the phenolic resin as embraeling novolac, polybenzylic ether, and resole resins. The three-component admixture is called a "binder." "Binder" is a term used in chemical art to mean a component of a composition primarily responsible for cohesive or adhesive forces. Column 7, lines 48-50, of the '579 patent states that the binders may be used as adhesives and coatings. Claim 1, in referring to its admixture, does not state that the admixture will react at room temperature, nor is there an implication that it will react quickly.

Claim 1 refers to the phenolic resin as "non-aqueous." Although the patent defines non-aqueous to mean "a phenolic resin which contains less than 5% of water and preferably less than 1% of water based on the weight of the resin," Col. 4, lines 63-66, Ashland contends that resins containing as much as 10% of water would be "non-aqueous" and therefore within the scope of Claim 1.

The only difference between Claims 1 and 13 of the '579 patent is Claim 13's requirement that a foundry binder be formed

using at least 90% sand. Claims 15, 16 and 18 are process claims that require that up to 10% of the binder described by Claim 1 be mixed with sand, the resulting mix be shaped, and the shaped mix be cured with a gaseous tertiary amine in a "cold box" process. This process, known commercially as "Isocure," is called a cold box process because the binder is cured without heating. Ashland's Isocure product uses a benzylic ether phenolic resin, as described in the '797 patent. When mixed with sand and cured with a gaseous amine, Isocure and its use are within the scope of Claims 1, 13, 15, 16 and 18 of the '579 patent.

The '392 Patent

Claim 1 of the '392 patent discloses a resin composition consisting of a phenolic resin, a hardener component, and a curing catalyst. The resin may be either a benzylic-ether type resin or an organic solvent soluble resole resin. The hardener is a polyisocyanate. The catalyst is "a base having a  $pK_b$  value in the range of about 7 to about 11." Claim 1 does not refer to a binder, but merely to a resin composition, with no expressed end use. The claim does not require the presence of solvents, nor does it require that the composition react at room temperature. Claims 1 and 16 of the '392 patent differ only in that Claim 16 requires that a foundry binder be formed using at least 90% sand.

As noted above, the Isocure cold box process involved a chemical admixture blown into the core box and a gassing of the mixture with the amine catalyst. In the "Pep Set" no-bake process of the '392 patent, on the other hand, an admixture of the resin and the polyisocyanate hardener is formed and the catalyst mixed with the sand before introduction into the core box. The chemicals then react with one another to cure the binder around the sand grains to form the core without further catalysis by heat or tertiary amine.

Pep Set is claimed to meet the foundry requirements of speed, precision, economics, absence of heat, "collapsibility,

shelf life, and core storage. It is also said to demonstrate an unusual property: after the resin, hardener, and catalyst are mixed with the sand, the binder remains substantially uncured for a finite, useful period of time. By varying the amount of catalyst, the length of time that the binder remains uncured can also be varied. While the binder remains uncured, the sand is completely flowable until after it is poured into the core box. Shortly after it is poured and shaped, the binder cures instantaneously and the core can be immediately stripped from the box and used. Plotting time against compressive strength on a graph, the Pep Set curing process forms an "S-curve." This property permits foundry workers enough time to form cores while running the core-making operation at high speed. Rapid use and re-use of core boxes allows a foundry to reduce its core-box inventory.

Delta's "Quick Set" binder system exhibits similar properties, but does not function as well, by Delta's own admission. For example, its S-curve is plotted about 10% to the left on a graph, showing that Quick Set has an inferior "work time/strip time" ratio.

#### File History

The application that led to the '579 patent was filed in the U.S. Patent Office on May 2, 1967. In the first Office Action, the examiner rejected all of the claims as being obvious in light of the prior "art," none of which showed tertiary amines to catalyze reactions between isocyanates and phenolic resins. Ashland's patent attorney, representing Dr. Robins, argued that the prior art failed to teach the use of a tertiary amine catalyst to accelerate the chemical crosslinking of a phenolic resin with an isocyanate. The '579 patent was granted without further argument. The patent examiner, however, did not consider the Shepard patent or any other prior art that showed tertiary amines to catalyze the reaction between phenolic resins and polyisocyanates.

Ashland's first patent application specifically claiming the '392 no-bake binder was Serial No. 723,873, filed April 24, 1968. When the application was filed, the claims were directed to the use of a catalyst comprising "a base having a  $pK_b$  value in the range of 4 to 13." On November 20, 1968, Ashland's attorney argued that the tertiary amines in the application that led to the '579 patent were not within the 4 to 13  $pK_b$  range of Serial No. 723,873, ignoring the fact that the 1967 application disclosed pyridine ( $pK_b$  = 9.0) as a catalyst. The attorney also argued that the tertiary amines employed in the parent application "are added to the mixture of the phenolic resin and the isocyanate after such mixture has been shaped to form the desired article."

In her March 16, 1970, Office Action, however, the examiner cited U.S. Patent No. 3,409,571 to Shepard. At Column 7, lines 43-44, Shepard refers to "N-methyl morpholine," which has a  $pK_b$  of 6.6. On June 15, 1970, Ashland's attorney responded that

" . . . Shepard et al relates to ordinary phenolic resin. It is further submitted that the disclosure at lines 41-43 of column 7 of Shepard does not render the present claims obvious because the teachings with respect to catalyzing methylol phenol resins and polyisocyanates does not logically apply to catalyzing benzylic ethermethylol phenolic resin and polyisocyanates. Moreover, this disclosure of Shepard et al does not teach a catalyst having a  $pK_b$  value of 4 to 13." (Emphasis added).

Application Serial No. 723,873 was abandoned for continuation application Serial No. 72,113 filed September 14, 1970. In 1971, patent application Serial No. 109,944 was filed with claims setting the  $pK_b$  value at "about 7 to about 11." The examiner did not cite the Shepard patent in either of the subsequent applications. The '392 patent issued from the 1971 application.

In 1974, Delta surveyed the foundry binder market to determine which products being sold offered the best chance for

easy market penetration. Ashland's Pep Set and Isocure were the only two products projected to double in sales. The Pep Set (phenolic urethane) market seemed to have the best growth prospects.

In autumn, 1975, Delta developed and offered for sale its "Quick Set" and "Cold Box" binder systems to compete with Pep Set and Isocure, respectively. At that time, Delta had knowledge of the Robins patents, but had not received any opinion as to whether its Quick Set and Cold Box products infringed them. Delta considered Pep Set the benchmark for Quick Set.

Ashland offered Delta a license under the patents in suit, which was rejected for economic reasons. On February 23, 1976, Ashland filed this suit against Delta alleging infringement of the Robins '579 and '392 patents.

#### Alleged Infringement

"[A] party asserting a patent's invalidity bears the burden of proving invalidity and must overcome by clear and convincing proof the presumption of validity established by 35 U.S.C. § 282." Laser Alignment, Inc. v. Woodruff & Sons, Inc., 491 F.2d 866, 871 (7th Cir. 1974), cert. denied, 419 U.S. 874 (1974). "The presumption of validity, however, does not exist against prior art which was not considered by the Patent Office when the patent was issued." Lee Blacksmith, Inc. v. Lindsay Bros., Inc., 605 F.2d 341, 342-343 (7th Cir. 1979).

Like Pep Set, Delta's Quick Set is a three-part system. It contains a phenolic resin, an isocyanate hardener, and a tertiary amine catalyst with a  $pK_b$  value in the 7 to 11 range. The first resin marketed as part of Quick Set was designated "248." Some of it contained more than 5% water, and so did not meet the definition of "non-aqueous" prescribed by the Robins patents. Other parts of the 248 resin, Delta admits, did contain less than 5% water, and infringed Claim 16 of the '392 patent, if that patent is valid.

Delta admits that part of its 248 resin infringed Claim 16 because at least some of it was a "methylol-terminated phenolic resin which comprises a resole resin which is organic solvent soluble" within the language of that claim. Ashland contends that the remainder of the 248 also infringes Claim 13 because it contained a "resole resin," a polyisocyanate, and a tertiary amine curing agent.

The 248 resin was marketed for only a short time. To avoid the infringement problem, Delta substituted its "629" resin for the 248. The 629 resin is 8-10% water. Later, Delta replaced 629 with its "645" resin, which apparently is about 2-3% water. In making these modifications, Delta made Pep Set its standard of binder quality. Even now, Delta believes that Quick Set with 645 resin does not perform as well as Pep Set.

As will be discussed later in this opinion, Delta argues that the prior art makes Ashland's patents invalid for obviousness under 35 U.S.C. § 103. In addition, Delta argues that neither the 629 nor the 645 resin used in Quick Set is a "methylol-terminated phenolic resin which comprises a resole resin which is organic solvent soluble." The dispute centers around the number of aromatic rings in the resins employed in the competing products. The claims in the Robins patents do not specifically define the molecular weight of the "phenolic resin" called for, although Claim 1 of the '579 patent does refer to a "condensation product" of phenol and formaldehyde that requires at least 2 rings per molecule.

Neither patent in suit specifically states the molecular weight or the average number of rings per molecule applicable to "resole resins," but they do define the preferred class of phenolic resins in terms of the average repeating aromatic rings per molecule. There is no suggestion that the range of molecule sizes given for the benzylic ether resins are inapplicable to resole resins.

In deposition, Dr. Robins said that the term "phenolic resin" was difficult to define. Ashland would define it in terms of its "method of manufacture" rather than the chemical identity of the constituent compounds because of the alleged difficulty in determining the many chemicals present in the reaction product of phenols and the aldehyde product. It argues that the reaction product is not just one distinct chemical compound, but instead a complex mixture of several different compounds. The mixture is said to vary in quantity and quality depending upon the precise conditions at time of manufacture. Ashland, then, would define a resole resin as a reaction of an excess of formaldehyde with phenol in the presence of an alkaline catalyst and heat.

Delta, on the other hand, prefers defining resins by chemical identity.

Both patents in suit refer to the Robins '797 patent for a more detailed description of the resins that they contemplate using. The '797 patent describes two classes of compositions: "adducts," the one and two-ring compounds shown by formulas A, B and C in Column 2, lines 30-50, and "resins," shown by the structural formula in Column 2, line 60, which requires at least 3 rings per molecule. At Column 3, line 53, the '797 patent states that "the molecular weight of the phenolic resins of the present invention can be varied widely and the degree of polymerization as measured by the number of benzene rings in the polymer molecule can vary from 4 to 40 and higher." This appears to show Dr. Robins' intention to use the number of rings per molecule to define the resins encompassed by the patents in suit. Moreover, at Column 4, line 26, the '797 patent refers to "normal resole resins" as having a molecular weight of 350, which would require an average of at least 3 rings per molecule.

In examining the application that matured into the '797 patent, the Patent Office refused to examine both the "adduct"

and "resin" claims in the same application, because they were directed to two separate inventions. In response, Ashland canceled its "adduct" claims and pursued the others.

At the bottom of Column 1, the '579 patent describes the resole resins as "polymers having a highly branched structure." A phenolic resin having a branched structure would require a minimum of 4 rings per molecule, while a highly branched structure would require 5 or 6. At the top of Column 4, the '579 patent further states that "phenolic resin" defines "any polymeric condensation product obtained by the reaction of a phenol with an aldehyde." A "condensation product" of a phenol and a formaldehyde would require at least 2 rings. A "polymeric condensation product" implies "poly" (or many) condensates, thus dictating an average of 3 or more rings per molecule. At Column 5, line 30, the '579 patent also refers to the application that matured into the '797 patent, which defines a resin as having an average of 4 to 40 rings per molecule.

The '392 patent, Column 1, line 55, describes resole resins as "polymers having a highly branched structure," thus requiring at least 4 rings per molecule, as above. At Column 3, line 29 et seq., the '392 patent also describes the resins as having "average degrees of polymerization, as measured by the number of repeating aromatic rings, of generally 3 to 100 and preferably 4 to 10." Column 3, line 60, of the '392 patent refers to the disclosure of the '797 patent.

The '392 patent, Column 4, line 72, states that it is feasible to use "low molecular weight resins." To remain consistent with the other teachings of that patent, this disclosure would seem to indicate the use of resins with an average of 3 to 4 rings per molecule. Example 11 of the '392 patent, however, is not so easy to distinguish. It refers to "benzylic ether resins," which have a molecular weight of 150-200 (indicating an average of 1.5 rings per molecule) but which are defined by the resins of

Formulas I, II and III. Those formulas appear to show at least 3 rings per molecule and a molecular weight of over 300, which is inconsistent with the disclosure of a 150-200 molecular weight. This isolated anomaly does not alter my conclusion that the '392 patent calls for resins with more than 3 aromatic rings.

Example 12 of the '392 patent offers an illustration of a resole resin. Both Ashland and Delta have tried and failed to reproduce the tensile strengths shown in the example. No evidence exists as to the molecular weight of the resin produced during the attempts to reproduce Example 12.

### Ordinary Skill in the Art

According to 35 U.S.C. § 103.

"A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. \* \* \*" (Emphasis added).

Ashland has argued that different levels of skill should apply in this case, because Delta has asserted defenses under both § 103 and 35 U.S.C. § 112. Section 112 states that

"The specification [i.e., patent] shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most clearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

"The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention."

Section 103 is intended to insure that inventions that are obvious derivations of prior patents are not patented. Section 112, on the other hand, seeks to insure that the inventor describe his

discovery clearly enough to allow others to "make and use" his teachings after the 17-year patent protection period has expired. Thus, §§ 103 and 112 are addressed to the same person, but at different times: § 103 before an attempt at patenting, and § 112 during the prosecution of the patent.

However, the § 103 person "having ordinary skill in the art" is the would-be inventor or the patent examiner, while the § 112 person "skilled in the art" is the scientific world to which a patent must be made clear. While the two sections address the skills of different persons, I find that they call for the same level of skill. Moreover, in terms of Delta's assertion that the prior art made the Robins patents obvious under § 103, Ashland's comparison of §§ 103 and 112 is a red herring. In considering whether a patent is obvious under § 103, the court need only determine whether the § 103 skill standards apply. Because I find that the §§ 103 and 112 skill standards are identical, however, the same standard will be applied to all of Delta's defenses under those two sections.

Each party presented a number of expert witnesses. Each expert varied in his level of education and training in chemistry. Ashland argues that Delta expert Marion Myers, who has a master's degree and experience in foundry chemical research, is a person of "ordinary skill," but that only people like its expert, Dr. Schafer, who has a doctorate and experience in foundry chemical research, have the "depth of knowledge" to discover what is nonobvious. I cannot agree. For all claims of the patents in suit, a person with a bachelor's degree in chemistry plus two years of research experience in phenolic and polyurethane chemistry, preferably with additional work with foundry binders, would appear to have "ordinary skill in the art." By this I do not mean to say that a person with that level of skill would necessarily be inventive. I do mean that such a person could have looked at the prior art to determine whether any discovery that

he might have made would be obvious in light of the prior art.  
See Popeil Bros., Inc. v. Schick Electric, Inc., 494 F.2d 162,  
167 (7th Cir. 1974).

Commercial Success

In Graham v. John Deere Co., 383 U.S. 1, 18-19 (1966),  
the Supreme Court stated:

"While the ultimate question of patent validity is one of law, \* \* \*, the § 103 condition [of nonobviousness], which is but one of three conditions, each of which must be satisfied, lends itself to several basic factual inquiries. Under § 103, the scope and content of the prior art are to be determined; differences between the prior art and the claims at issue are to be ascertained; and the level of ordinary skill in the pertinent art resolved. Against this background, the obviousness or nonobviousness of the subject matter is determined. Such secondary considerations as commercial success, long felt but unsolved needs, failure of others, etc., might be utilized to give light to the circumstances surrounding the origin of the subject matter sought to be patented. As indicia of obviousness or nonobviousness, these inquiries may have relevancy."

The Graham analysis is the only measure of obviousness under § 103. Republic Industries, Inc. v. Schlage Lock Co., 592 F.2d 963 (7th Cir. 1979). Secondary considerations such as commercial success "may be weighed only in a close case, in which the application of the primary criteria of nonobviousness under section 103 does not produce a firm conclusion. . . ." Id. at 975.

The parties have agreed that Ashland's Pep Set and Isocure products are a commercial success, although they dispute whether Ashland receives significant royalties from licensees. However, for reasons that will be made clear, the "primary criteria of obviousness" warrant a finding of the obviousness of the Robins patents. Furthermore, Ashland has never sold any Pep Set or Isocure materials containing anything other than benzylidene type resins. The prior art that Delta relied upon to develop its binders described the use of both resole and novolac

resins, but not benzylic-ether resins. Proof of commercial success based on benzylic-ether resins does not overcome prior art that shows the obviousness of resole and novolac resins. The evidence at trial indicated that resole resins per se were not readily usable in the claimed invention. Therefore, I do not believe this a case close enough to merit the weighing of secondary considerations. Commercial success will not make valid an otherwise obvious patent. Anderson's-Black Rock, Inc. v. Pavement Salvage Co., Inc., 396 U.S. 57, 61 (1969). "Commercial success, of course, may be achieved by diligent huckstering and in that event would have no bearing whatsoever on the question of obviousness." Lee Blacksmith, supra at 347 (Pell, J., dissenting).

#### The Prior Art

In Popeil Bros., supra at 167, the Seventh Circuit stated that

"The defense of obviousness challenges the inventiveness of the purported invention rather than, as with anticipation, its novelty. The question to which the defense addresses itself is whether on the basis of the determined differences between prior art and the claims at issue 'a hypothetical person having ordinary skill in the art would have found the same solution when addressing himself to the same problem.' \* \* \* This requirement is less stringent than the substantial identity between prior art and the purported invention which is required to find anticipation. Thus prior art which is insufficiently similar to anticipate a purported invention may still render it obvious. \* \* \* Where, however, a purported invention is anticipated by prior art, it cannot be disputed that it must also be obvious." (Citations omitted).

Because I find that the Robins patents are obvious in light of the prior art, it will not be necessary to deal with the question of anticipation under 35 U.S.C. § 102.

Dr. Robins' '579 patent states that "it has been known heretofore that isocyanates react with phenolic resins to result in cross-linked materials." Nevertheless, the patent stated that "heating has generally been employed to cause the isocyanate to

react with the phenolic resin either through the phenolic hydroxyl group or through the methylol group in order to achieve the formation of cross-linking urethane bonds." This "cross-linking" would appear to require the reaction of a polyisocyanate and a phenolic resin to form a "thermoset" or insoluble product.

Prior to 1965, when Dr. Robins began working for Ashland, it was known that the reaction between polyisocyanates and phenolic resins could be accelerated by certain catalysts, including tertiary amines. For example, at page 75 the Saunders & Frisch treatise Polyurethanes--Chemistry and Technology (Exhibit 320A) states that "one normally uses a catalyst such as a tertiary amine" to accelerate reactions between phenols and isocyanates.

U.S. Patent No. 3,242,107 to Bunge et al. (Exhibit 314), filed in 1960, states that catalysts may be used in lieu of heating to accelerate the reaction of phenol formaldehyde resins and organic polyisocyanates. The patent does not state that the compositions could be used as foundry sand binders, although protective coatings and rigid foams would be produced.

U.S. Patent No. 3,043,794 to Feiler et al. (Exhibit 315), filed in 1962, describes the reaction of soluble phenolic resins with polyisocyanates in the presence of such tertiary amine catalysts as triamyl amines. The Feiler patent states the use of both novolac-type and resole-type phenolic resins, and uses the phenolic resin-isocyanate reaction products to bond together layers of laminating materials. Heating is suggested to remove solvents. The tertiary amine catalyst is present to promote the isocyanate-phenolic resin reaction. The patent does not disclose use of the compositions as foundry sand binders, but rather as an insulating varnish. No gassing to cure is shown.

U.S. Patent No. 3,409,571 to Shepard et al. (Exhibit 317), filed in 1964, was described by Delta's expert, Dr. Wendland,

as one of the two most pertinent references in the prior art. It describes a novolac-type phenolic resin modified with a phosphorous compound to make it fire-resistant. The resulting phosphate esters are soluble thermoplastics. It appears that basic novolac-resin characteristics remain after the phosphorous modification, and that many of the phenolic hydroxyl groups remain available for later crosslinking with isocyanate. As noted earlier, Ashland's attorney, when prosecuting the Robins patents, stated that the Shepard patent related to "ordinary phenolic resins" as distinguished from benzylic-ether phenolic resins. The Shepard patent describes crosslinking the modified phenolic resins with polyisocyanates, with the option of using tertiary amine catalysts, such as N-methyl morpholine, to accelerate the crosslinking. Shepard suggests using the thermosetting compositions as foundry sand binders, and the polyurethane compositions as foamed products, castings, coatings, and the like.

U.S. Patent No. 3,398,122 to Shepard *et al.* (Exhibit 317-A), filed in 1964, is similar to Shepard Patent 3,409,571 above, but the '122 patent describes modification of phenolic resins with a silicon or similar compound to improve the phenolic resin's fire resistance. The modified phenolic resins, according to Column 8, may be crosslinked with polyisocyanates. Tertiary amine catalysts, such as N-methyl morpholine, may be used to accelerate the crosslinking. At Column 9, line 5, the compositions are said to be useful as foundry sand binders.

U.S. Patent No. 3,282,896 to Einberg (Exhibit 330), filed in 1963, teaches the formation of polyurethanes by reacting polymethylol phenols (one-ring phenolic compounds) with polyisocyanates in the presence of tertiary amine catalysts. Useful resins may be made by reacting diisocyanates with dimethylol phenols or the para-substituted dimethylol phenols. The resulting polyurethane resins are said to be useful for protective

coatings (such as varnishes), potting compounds, and rigid foams. Einberg does not suggest use of the varnish as a foundry binder.

British Patent No. 1,031,909 to the General Electric Company (Exhibit 313), published in 1966, was based on a British "Complete Specification" filed in 1963, which in turn was based on U.S. Patent Application Serial No. 241,131 (Exhibit 313-A), filed in 1962. The British patent teaches the use of a novolac resin, not an organic solvent soluble resin as required in the Robins '392 patent. There is no disclosure that a tertiary amine catalyst could be used. However, the British patent does describe polyurethanes as thermoset compositions and specifically claims them as "binders for sand, asbestos, carborundums and paper constituted by a thermoset condensation product."

Ashland argued that the prior art fails to describe the inventions claimed in the '579 and '392 patents because the prior art requires heat to cure the phenolic resin-isocyanate reaction products even when catalysts are used. While the language of the claim must be read in light of the specification and the file wrapper, Graham, supra at 33; United States v. Adams, 383 U.S. 39, 48-49 (1966), the claim alone is the measure of the invention. Aro Mfg. Co. v. Convertible Top Replacement Co., 365 U.S. 336, 339 (1965); Laser Alignment, supra at 872. The claims of the patents in suit do not exclude the use of heat, nor do they require that the compositions be reactable at room temperature. Many of the systems described by the prior art use heat to remove solvents. The heat would promote the reaction between the isocyanate and the phenolic resin, but the amine catalyst would not contribute to the solvent removal. The catalyst's only function would be to accelerate the reaction.

Ashland also contends that, unlike the Robins patents, the prior art does not make "admixtures" because, in some places, it teaches a partial reaction of the phenol and polyisocyanate, which is later mixed with tertiary amines to catalyze the final

reaction. However, Dr. Schafer, one of Ashland's experts, testified that the phenolic resin and polyisocyanate were similarly pre-reacted in the cold box process prior to curing with the amine catalyst. Even without such an admission, I am not persuaded that a significant difference exists between the partial reactions of the prior art and the "admixtures" of the patents in suit.

The subject matter of Claim 1 of the '579 patent and that of the prior art, particularly the Shepard patents, appears to be substantially the same. Shepard describes a phenolic resin (however modified) that includes a plurality of phenolic hydroxyl groups and polyisocyanates used to crosslink that resin. The polyisocyanates react with the phenolic hydroxyl groups to crosslink the phenolic resins with urethane linkages. Shepard also teaches the use of tertiary amines to accelerate the crosslinking, and discloses foundry binders based on crosslinked phenolics. It describes three agents to crosslink the phenolic resin, one of which is polyisocyanate. One skilled in the art reading the entire disclosure would conclude that the Shepard patent thus taught phenolic-urethane foundry binders.

Shepard's attorney presented an "Abstract of the Disclosure" of the Shepard '571 patent, which appears at Column 1, to the U.S. Patent Office. Although the Abstract is not conclusive, especially because it was submitted several years after the filing date, it was filed by a party with no interest in the present lawsuit and provides a neutral aid to interpretation of the Shepard patent. At Column 1, line 38, the Abstract reads, "Thermosetting products can be produced by curing the thermoplastic products with agents such as hexamethylene-tetramine, or other donors of methylene radicals or polyepoxides, or polyisocyanates, and the like" (emphasis added). Thus, the Abstract places polyurethanes in the class of "thermosetting" compositions, which are said to be useful as foundry binders.

The Shepard '571 patent, especially when viewed along with the British patent, describes phenolic urethanes as thermoset materials that can be used as foundry binders. The Shepard patent also teaches the use of the tertiary amine catalysts to enhance the reaction between the polyisocyanate and the phenolic resin. Thus, the prior art makes Claim 13 of the Robins '579 patent obvious. Claims 15, 16 and 18 were also made obvious by the Shepard patents and the British patent, and the prior art that taught the use of a wide variety of tertiary amines, including some gaseous amines, to make polyurethanes.

The second subset of prior art before the court involves the dispute over the  $pK_b$  range of the tertiary amines used as catalysts in the binder system. Prior to 1965, the chemistry of polyurethane chemistry had been extensively studied. A wide variety of catalysts had been investigated and used to accelerate the formation of urethanes, which are formed in the reaction between isocyanates and such hydroxyl-containing materials as phenols. The tertiary amines, including those having "a  $pK_b$  value in the range of about 7 to about 11" as prescribed in the Robins patents, were described in the prior art as catalysts to accelerate such urethane-formation reactions. Pyridine, which has a  $pK_b$  value of about 9.0, was one of the more frequently described tertiary amines. As noted above, the application that led to the '579 patent called for a 4 to 13  $pK_b$  range, while the '392 patent called for a 7 to 11 range.

Saunders & Frisch, whose treatise (Exhibit 320) was published in 1962, refer at page 139 to work by Baker in the 1940s that compared the catalyst strength to the base strength for tertiary amines in the urethane-forming reaction, including many catalysts in the  $pK_b$  range of "about 7 to about 11." The use of pyridine,  $pK_b = 9.0$ , is also taught by U.S. Patent No. 2,957,832 to Gmitter *et al.* (Exhibit 321), filed in 1956; U.S. Patent Nos. 3,173,896 (Exhibit 322) and 3,173,897 (Exhibit 323).

both to Adams et al., filed in 1960; and U.S. Patent No. 3,265,666 to Brown (Exhibit 324), filed in 1961.

U.S. Patent No. 2,906,717 to Sekmakas (Exhibit 316) describes the crosslinking of phenolic resins with organic polyisocyanates, using N-methyl morpholine as a catalyst. The Shepard patents, of course, also call for the use of N-methyl morpholine. As noted earlier, N-methyl morpholine's  $pK_b$  value is about 6.6. Dr. Schafer, Ashland's expert, testified that that value would be within the range of "about 7 to about 11." Sekmakas discloses processes producing either novolac-type phenolic resins or resole-type phenolic resins. His patent states that various tertiary amines may be used to catalyze crosslinking reactions. His compositions are stated to result in cellular plastic foams, with good adhesive qualities. According to trial testimony, if the foaming agent--water--were omitted, the reaction would produce a solid polyurethane. Such a teaching could have been used by Delta in the development of 645, its "low water" resin.

U.S. Patent No. 3,156,659 to Robitschek (Exhibit 331), filed in 1964, describes polyurethane binders produced from both one-ring phenolics and two-ring phenolics, which are reacted with polyisocyanates using tertiary amine catalysts such as N-methyl morpholine. These catalysts are used to promote the reaction of the isocyanate with the hydroxyl compounds.

U.S. Patent No. 3,063,964 to Khawam (Exhibit 325), filed in 1962, describes a trimethylol phenol (a one-ring phenol) that is reacted with a polyisocyanate in the presence of a tertiary amine catalyst, such as N-alkyl morpholine. The N-alkyl morpholines include N-ethyl morpholine, which was tested by Dr. Robins, and N-methyl morpholine. N-ethyl morpholine, like N-methyl morpholine, has a  $pK_b$  value of 6.6, within the  $pK_b$  range of "about 7 to about 11" prescribed by Dr. Robins. Khawam further described the use of polyether glycols with the polymethylol phenols. Dr. Schafer stated that these materials would react to

form a polyurethane, and that an S-curve would result if the right amine were used.

Therefore, Claim 1 of the Robins '392 patent seems obvious in light of the prior art. That claim teaches a restricted group of catalysts, those with a  $pK_b$  value "in the range of about 7 to about 11." The Shepard patents, and those of Khawam, Robitschek, and Sekmakas all teach catalysts in that  $pK_b$  range. While the '392 patent specification contemplates an end use of foundry sand binders, no such use is addressed in its claims.

The claims of a patent measure the scope of the grant. Laser Alignment, supra at 872. "The monopoly granted to the inventor can never be broader than the invention disclosed to the public, and while the specification and the file wrapper may limit a claim or serve to resolve an ambiguity in it, they may not be used to enlarge the claim." Super Products Corp. v. D P Way Corp., 546 F.2d 748, 757 (7th Cir. 1976).

Similarly, the prior art appears obvious over Claim 16 of the '392 patent. The Sekmakas, Feiler and Bunge patents teach the equivalency of the novolac-type phenolics for reactions with polyisocyanates. One skilled in the art of phenolic resins could readily sense that a resole resin might be substituted for a novolac. Furthermore, Dr. Schafer testified at trial that in 1965 it would have been obvious to those skilled in the art to apply the Saunders & Frisch teachings of polyurethane catalysis to the phenolic resin-isocyanate systems described by the '579 patent. The Robins '579 patent suggests the equivalency of the novolac and resole resins with respect to preparing isocyanate crosslinked polyurethanes. Based on the prior art, it would be obvious to one of ordinary skill in the art to substitute resole resins of the type defined by the Sekmakas, Feiler and Bunge patents for the novolacs described in the Shepard patents. Shepard clearly teaches that foundry binders can be produced from phenolic urethanes cured with catalysts in the  $pK_b$  range later selected by Robins. Therefore, it would be obvious to one of

ordinary skill to substitute a resole resin for a novolac resin, and to produce foundry binders accordingly. This would be no more than "selecting the last piece to put into the last opening in a jig-saw puzzle." Sinclair & Carroll Co. v. Interchemical Corp., 325 U.S. 327, 335 (1945).

The Khawam patent also shoots down Ashland's contention that the prior art does not teach the S-curve achieved by Ashland's Pep Set binder system. While the prior art does not appear to teach that the foundry binders would react instantaneously, as do Pep Set and Delta's Quick Set, the claims of the patents in suit do not exclude slow-acting binders, nor do they appear to exclude binders that produce a relatively low tensile strength.

Pertinent prior art in evidence before me was not before the U.S. Patent Office in the prosecution proceedings involving the Robins '579 and '392 patents. "The [35 U.S.C. § 282] presumption of validity. . . does not exist against prior art which was not considered by the Patent Office when the patent was issued." Lee Blacksmith, supra at 342-43. "Even one prior art reference not considered by the Patent Office can suffice to overcome the presumption." Scott Paper Co. v. For Howard Paper Co., 432 F.2d 1198, 1203 (7th Cir. 1970). The fact that a prior art device was not commercially successful does not render it any less valid as a prior art reference against the patent claims in suit. Endevco Corp. v. Chicago Dynamic Indus., Inc., 268 F. Supp. 640, 650 (N.D. Ill. 1967).

Patent applications pending in the Patent Office at the time a second application is filed constitute part of the prior art within the meaning of 35 U.S.C. § 103. Hazeltine Research, Inc. v. Brenner, 382 U.S. 253 (1965). Therefore, Shepard Patents Nos. 3,409,571 and 3,398,122 are available as prior art against the Robins patents. British Patent No. 1,031,909 and the U.S. application upon which it is based also qualify as persuasive evidence that the subject matter of the claims in suit were

obvious within the meaning of § 103. Popeil Bros., supra at 166-167 (Japanese technical publications); Faldburn v. New York Central R.R. Co., 350 F.2d 416, 425 (6th Cir. 1965) (German technical publications); All States Plastic Mfg. Co., Inc. v. Weckesser Co., Inc., 362 F. Supp. 94, 100-101 (N.D. Ill. 1973), aff'd 506 F.2d 463 (7th Cir. 1974); Amerline Corp. v. Cosmo Plastics Corp., 271 F. Supp. 215, 224, 227 (N.D. Ill. 1967), aff'd 407 F.2d 666 (7th Cir. 1969) (German patent).

#### Double Patenting

"No patent can issue for an invention actually covered by a former patent, especially to the same patentee, although the terms of the claims may differ." Miller v. Eagle Mfg. Co., 151 U.S. 186, 198 (1894). "The principal reason for prohibiting double patenting is to prevent inventors from getting more than the 17 year monopoly on one invention. An extension of a monopoly, is only justified by the presence of an invention which grants the second application as much dignity as the first." Weatherhead Co. v. Drillmaster Supply Co., 227 F.2d 98, 102 (7th Cir. 1955). Double patenting relates only to what the patent claims, not what it discloses. In re Aldrich, 398 F.2d 855 (C.C.P.A. 1968). The inventor's own patent disclosure cannot be used as "prior art" against him. In re Bovlan, 392 F.2d 1017 (C.C.P.A. 1968). However, the patent disclosure may be used as a "dictionary" to learn the meaning of terms in a claim, or to shed light on the question of obviousness. In re Vogel, 422 F.2d 438, 441 (C.C.P.A. 1970). In a double-patenting dispute, it is customary to examine the first patent's specifications to determine the meaning of the terms used in its claims. See, e.g., In re Bushler, 515 F.2d 1134, 1141 (C.C.P.A. 1975).

Therefore, it is proper to look to the '579 patent specification to determine whether the '392 (no-bake) patent is an obvious variation. Delta contends that the specification of Claim 1 of the '579 patent allows for the use of such liquid

tertiary amines as pyridine as well as the gaseous amines taught in the process claims. In other words, the test of double patenting in this case is whether the '392 claim specifying the catalyst with a  $pK_b$  value in the range of 7 to 11 is a nonobvious variation on the claim of the '579 patent, which specifies pyridine ( $pK_b = 9.0$ ) as a tertiary amine catalyst. The following table makes clear the lack of significant difference between the two Robins patents:

<u>Claim 1 of '579</u>	<u>Meaning per '579 specification</u>	<u>Claim 1 of '392</u>
binder composition	binders may be used as "adhesives and coatings" (Col. 7, lines 49-50)	resin composition comprising in admixture
comprising in admixture		
resin component; hardener component; curing agent		phenolic resin component; hardener component; curing catalyst
resin is a solution of "a condensation product of a phenol . . . with an aldehyde"	phenolic resins include resole or novolac resins (Col. 4, line 55) or polybenzyllic ether resins (Col. 5, lines 12-45)	resin is either (a) a soluble benzyllic ether resin, or (b) a soluble resole resin
hardener is a liquid polyisocyanate		hardener is a liquid polyisocyanate
and a curing agent comprising a tertiary amine	tertiary amines include pyridine ( $pK_b = 9.0$ ) (Col. 7, line 51)	and a curing agent is a base having $pK_b$ value of 7-11

#### Claim 13 of '579

"A foundry mix containing sand as the major constituent and a binding amount of up to 10% based on the weight of sand of the binder of Claim 1."

The scope of the claims of the two patents varies slightly, but the '392 patent is an obvious variation of the invention disclosed and claimed in the '579 patent. Therefore, it represents an unlawful attempt to extend the monopoly of that patent.

#### Claim 16 of '392

"A foundry mix containing sand as the major constituent and a binding amount of up to 10 percent based on the weight of sand of the resin composition of Claim 1."

Furthermore, by asserting that a single Delta product infringes the claims of both patents, Ashland has waived any contention that the claims do not overlap. Plax Corp. v. Precision Extruders, Inc., 239 F.2d 792, 796 (3rd Cir. 1957); see Plax Corp. v. Elmer E. Mills Corp., 204 F.2d 302, 307-308 (7th Cir. 1953).

#### Non-Infringement

Even if the prior art had not made the Robins patents obvious, Ashland cannot prove infringement. The '579 and '392 patents call for a minimum of 3 to 4 repeating aromatic rings per molecule in the resins specified. The 629 and 645 phenolics that Delta uses in Quick Set, however, have low molecular weights -- their average degree, measured by the number of repeating aromatic rings per molecule, is about 1.5, based on Ashland's own nuclear magnetic resin (NMR) spectra. The high-pressure liquid chromatography (HPLC) analysis offered by Delta, which shows that the 629 and 645 phenolics were predominantly one-ring compounds, is consistent with the NMR analysis.

I also find Delta's method of defining a "resole resin" more persuasive than Ashland's. Ashland contends that a resole resin should be defined by the process by which it is made. The Robins patents, however, describe resins in terms of the structure of the resin molecule. Both the Einberg (Exhibit 330) and Khawam (Exhibit 325) patents describe one-ring phenolic compounds, which Ashland argues are not "resins," made by heating excess formaldehyde with phenol in the presence of an alkaline catalyst. Both Einberg and Khawam refer to the work of Martin--U.S. Patent Nos. 2,579,329 (Exhibit 326), 2,579,330 (Exhibit 327), and 2,579,331 (Exhibit 328), all filed in 1951; and U.S. Patent Nos. 2,598,406 (Exhibit 329-A), 2,606,929 (Exhibit 329-B), and 2,606,935 (Exhibit 329-C), all filed in 1952--which describes low molecular weight one-ring compounds produced by combining an excess of formaldehyde with phenol in the presence of an alkaline catalyst and heat.

During the prosecution of the application (Exhibit 309) that led to the '392 patent, Ashland's attorney told the patent examiner that the Einberg patent did not describe a resin, despite Einberg's reference to the Martin patents. The examiner rejected the proposed amendment to the application, and thus there was no "file wrapper estoppel" based on Ashland's argument. Cf. Graham, supra at 33. However, a line of cases has developed an estoppel theory broader than the traditional file wrapper estoppel, which applies only to amendments. Moore Business Forms, Inc. v. Minnesota Mining & Mfg. Co., 521 F.2d 1178 (2d Cir. 1975); Duplan Corp. v. Deering Milliken, Inc., 379 F. Supp. 388 (D. S.C. 1974) (court reversed itself on application of traditional file wrapper estoppel and applied estoppel by admission); Marston v. J. C. Penney Co., Inc., 324 F. Supp. 889 (E.D. Va. 1971), aff'd mem., 469 F.2d 694 (4th Cir. 1972); William Hedges & Co. v. Starwood Corp., 348 F. Supp. 383 (E.D. N.Y. 1972) (dicta). "A patentee having argued a narrow construction for his claims before the [Patent Office] should be precluded from arguing a broader construction for the purposes of infringement." Coleco Indus., Inc. v. United States Int'l Trade Comm'n, 573 F.2d 1247, 1257 (C.C.P.A. 1978). Therefore, I consider the proposed amendment reliable evidence that the process of reacting excess formaldehyde with phenol in the presence of an alkaline catalyst and heat can produce something other than a "resin."

Even greater weight may be accorded Ashland's restriction on claims during the prosecution of the application that matured into the Robins '797 patent, which was referred to in the patents in suit. In that application, as noted above, Ashland distinguished "resins" with 4 to 40 benzene rings from one-ring phenolic materials. The claims were allowed on that basis. Because Dr. Robins referred to the '797 patent for the definition of "resin" he used in the '579 and '392 patents, Ashland should not be heard to assert a different definition here. Claims must be construed on the same basis as they were presented to the Patent

Office, and any claims for subject matter that have been abandoned or surrendered may not be reasserted at trial. See Exhibit Supply Co. v. Ace Patents Corp., 315 U.S. 126, 136-137 (1942); Coleco Indus., supra.

Similarly, the fact that Ashland distinguished one of the applications leading to the '392 patent from the disclosure of the Shepard '571 patent evinces Ashland's belief that the "ordinary phenolic resin. . . disclosure of Shepard et al does not teach a catalyst having a  $pK_b$  value of 4 to 13." That application, Serial No. 723,873, was abandoned for continuation application Serial No. 72,113. As noted earlier, another application in the '392 patent series, Serial No. 109,944 was filed with claims setting the  $pK_b$  value at "about 7 to 11." This shows Ashland's intent to insure that the patent examiner distinguish its claims from those in the Shepard patent, and it is precluded from arguing to the contrary here. Coleco, supra.

I also find that the requirement of Claim 1 of the '579 patent that the phenolic resin used be "non-aqueous"--containing "less than 5% of water and preferably less than 1%"--excludes the use of the high-water phenolics employed by Delta in Quick Set. This exclusion would extend at least to parts of the 248 phenolic and all of the 629 phenolic.

Therefore, I find that the 629 and 645 phenolics used in Quick Set do not infringe any of the claims of the patents in suit. Although Delta has admitted that some of its 248 included a "resin" within the scope of the claims of the patents in suit, my holding that the Robins patents are invalid makes that admission irrelevant.

Ashland has also not sustained its burden of proving infringement of the '579 patent by Delta's experimental "Cold Box" product. Cold Box was produced with a phenolic component called 248, purchased from Plenco. No evidence was placed in the record as to the actual nature of Plenco's 248, other than that its water content varied widely. Furthermore, there is no evidence that Delta ever sold Cold Box.

Ashland has also maintained that infringement can be shown under the doctrine of equivalents, even without literal infringement. Under the doctrine, a court must determine whether the accused product performs in substantially the same manner as the claimed product. The different molecular weights of the phenolics used in the products make them substantially different. Delta's monomeric materials, unlike Ashland's polymeric materials, react with polyisocyanates to form polyurethanes that do not include phenolic resins of 4 to 10 rings per molecule. Witnesses for both parties also testified that Pep Set and Quick Set perform differently.

In addition, no charge of infringement of the claims of patents relating to the benzylic-ether resins used by Ashland has been made. Delta appears to have developed its own technology in creating Quick Set. Therefore, there is no infringement under the doctrine of equivalents.

#### Conclusion

In light of my decision that the Robins patents were obvious variations of the prior art, and that the '392 patent was an obvious variation of the '579 patent, it is unnecessary to determine whether Claims 1 and 13 of the '579 patent were anticipated by the prior art under 35 U.S.C. § 102. It is also unnecessary to determine whether the '392 patent is invalid because of Dr. Robins' alleged failure to disclose the "best mode" of carrying out the supposed invention as required by 35 U.S.C. § 112. Similarly, I am not compelled to decide whether Ashland placed the "invention" taught by the '392 patent "on sale" more than one year prior to the filing date of the patent application in violation of 35 U.S.C. § 102.

Delta has requested treble damages and attorneys' fees, pursuant to 35 U.S.C. § 285. It considers this case "exceptional" in light of Ashland's conduct before the Patent Office and supposedly "unjustifiable refusal" to admit that its claimed inven-

tions were obvious variations of the prior art. Perhaps because of the expert performance by the attorneys for both parties, however, this was not an easy case to decide. Despite the weight of the prior art, the issues of patentability and infringement are sufficiently debatable to counsel against an award of treble damages and attorneys' fees. See Wahl v. Carrier Mfg. Co., 511 F.2d 209, 214 (7th Cir. 1975).

Therefore,

1. Claims 1, 13, 15, 16 and 18 of U.S. Patent No. 3,409,579 to Robins, and Claims 1, 13 and 16 of U.S. Patent No. 3,676,392 to Robins are invalid for obviousness under 35 U.S.C. § 103.

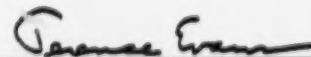
2. U.S. Patent No. 3,676,392 to Robins is invalid for double patenting as an obvious variation of invalid U.S. Patent No. 3,409,579 to Robins.

3. Defendant's request for treble damages and attorneys' fees under 35 U.S.C. § 285 is denied.

4. In light of this decision, Mr. Tittel and Mr. Egan are ordered to confer and determine, jointly if possible, what further proceedings will be necessary to bring this case to its conclusion. A report from both counsel suggesting the further direction of this litigation at this level must be filed within 30 days.

SO ORDERED at Milwaukee, Wisconsin, this 26  
day of March, 1981.

BY THE COURT:

  
TERENCE T. EVANS  
UNITED STATES DISTRICT JUDGE

CV 32  
17/83

## JUDGMENT ON DECISION BY THE COURT

4/24/81

Copy made available to the parties by the Court pursuant to Rule 77(d), Federal Rules of Civil Procedure.

United States District Court at 10 o'clock A.M.  
RUTH W. LEAVY, CLERK.

FOR THE

## EASTERN DISTRICT OF WISCONSIN

CIVIL ACTION FILE NO. 76-C-131

ASHLAND OIL, INC..

vs.

DELTA OIL PRODUCTS CORPORATION

JUDGMENT

This action came on for trial before the Court, Honorable TERENCE T. EVANS  
United States District Judge, presiding, and the issues having been duly tried  
and a decision having been duly rendered.

It is Ordered and Adjudged that Claims 1, 13, 15, 16 and 18 of U.S. Patent No. 3,409,579 to Robins, and Claims 1, 13 and 16 of U.S. Patent No. 3,676,392 to Robins are invalid for obviousness under 35 U.S.C. § 103; that U.S. Patent No. 3,676,392 to Robins is invalid for double patenting as an obvious variation of invalid U.S. Patent No. 3,409,579 to Robins; and that defendant's request for treble damages and attorneys' fees under 35 U.S.C. § 285 be denied.

It is further Ordered that the antitrust and misuse issues, at the request of the parties, be permanently stayed pending disposition of the appeal on this judgment that the plaintiff will soon perfect.

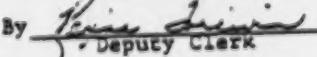
Approved as to form:

  
U. S. District Judge

Dated at Milwaukee, Wisconsin , this 24th day  
of April 1981.

SOFRON B. NEDILSKY

Clerk of Court

By   
Deputy Clerk

**FILED**

MAY 1 - 1981

Copy mailed to attorneys for parties by the Court pursuant to Rule 77(d), Federal Rules of Civil Procedures.

## JUDGMENT ON DECISION BY THE COURT

United States District Court

at o'clock M  
BUIN, W. CLERK

FOR THE

## EASTERN DISTRICT OF WISCONSIN

CIVIL ACTION FILE NO. 76-C-131

ASHLAND OIL, INC..

vs.

AMENDED  
JUDGMENT

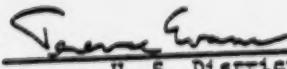
DELTA OIL PRODUCTS CORPORATION

This action came on for trial before the Court, Honorable TERENCE T. EVANS, United States District Judge, presiding, and the issues having been duly tried and a decision having been duly rendered.

It is Ordered and Adjudged that Claims 1, 13, 15, 16 and 18 of U.S. Patent No. 3,409,579 to Robins, and Claims 1 and 16 of U.S. Patent No. 3,676,392 to Robins are invalid for obviousness under 35 U.S.C. § 103; that U.S. Patent No. 3,676,392 to Robins is invalid for double patenting as an obvious variation of U.S. Patent No. 3,409,579 to Robins; that defendant's Quick Set product made with 629 and 645 phenolics does not infringe any of the claims of the patents-in-suit; that defendant's Quick Set product made with the high-water phenolic does not infringe the claims of U.S. Patent No. 3,409,579 to Robins; that defendant's experimental "Cold Box" product does not infringe the claims of U.S. Patent No. 3,409,579 to Robins; and that defendant's request for treble damages and attorneys' fees under 35 U.S.C. § 285 be denied.

It is further Ordered that the antitrust and misuse issues, at the request of the parties, be permanently stayed pending disposition of the appeal on this judgment that the plaintiff will soon perfect. The court has directed the Clerk to enter judgment as to fewer than all of the claims in the litigation upon the express determination that there is no just reason for delay in doing so.

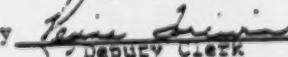
Approved as to form:

  
\_\_\_\_\_  
U. S. District Judge

Dated at Milwaukee, Wisconsin  
of May , 1981.

, this 7<sup>th</sup> daySOPRON B. NEDILSKY

Clerk of Court

By   
Deputy Clerk

1 the exhibit identified, that you don't have to make any  
2 offer of the exhibit into evidence, nor do you have to make  
3 any objection to it. And at the conclusion of the trial I  
4 will receive in evidence every exhibit that has been  
5 identified unless there's an objection at that point to it.  
6 I've found that many times even objections that you list in  
7 the pre-trial report after all the evidence is in there's  
8 really no significant objection. That avoids hassling over  
9 each one as we go along. So that will be the procedure  
10 we'll use here unless any of you have a strenuous objection  
11 and want to argue the point.

12 MR. EGAN: That's fine, Your Honor.

13 MR. TITTEL: Sounds fine.,

14 THE COURT: Okay.

15 DIRECT EXAMINATION

16 BY MR. TITTEL:

17 Q. Please state -- you've already stated your full name?

18 A. Yes.

19 Q. Where do you reside?

20 A. In Worthington, Ohio, a suburb of Columbus.

21 Q. By whom are you employed?

22 A. Ashland Chemical Company.

23 Q. Would you give us a resume of your education above  
24 the high school level, please?

25 A. I have a chemical engineering degree from the

1 University of Detroit, a Master's degree in metallurgy from  
2 Case Institute of Technology in Cleveland, Ohio and a  
3 Doctor's degree in metallurgy from the same institute.

4 Q. Would you please trace your employment history from  
5 the time you began working to the present time, please?

6 A. During my college years I worked at Ford Motor  
7 Company in the Dearborn iron foundry as a foundry trainee.

8 After graduating from the University of Detroit  
9 I worked for NASA, which was then called NACA, in  
10 metallurgical research.

11 Upon leaving NASA, I joined Archer Daniels  
12 Midland Chemical Division and was the research manager for  
13 the foundry products area up until 1968. In 1968 I became  
14 the development manager for what was then the Foundry  
15 Products Division of Ashland Chemical Company. About 1973  
16 I became technical director of the Foundry Products  
17 Division. In 1976 I became the group manager of a New  
18 Products Development group. In 1978 I became  
19 vice-president of the Chemical Systems Division and for the  
20 last six months I have been a research manager in the  
21 Avenger research department for Ashland Chemical Company.

22 Q. Approximately when was it that Ashland acquired the  
23 portion of Archer Daniels Midland Company pertaining to  
24 foundry binders?

25 A. In the spring of 1967.

1 Q. Are you familiar, Doctor Schafer, with the general  
2 history of the art of metal casting?

3 A. Yes, I am.

4 Q. Could you kind of provide for the Court a brief  
5 description of the art of making castings say, up to the  
6 time of — oh, the Second World War?

7 A. The casting industry predate written history  
8 starting sometime before 3500 B. C. That age from about  
9 3500 B. C. till around 1000 B. C. was known as the Bronze  
10 Age because the chief implements of protection and tools of  
11 commerce were made with cast bronze. The Bronze Age was  
12 followed by the Iron Age where iron became the primary cast  
13 item of both weaponry and tools of commerce. Through the  
14 ages the countries or the people that controlled the  
15 knowledge of the casting of metals were the most powerful  
16 people in the world, and in the Napoleonic times William  
17 Manchester, who's written a book on the Krupp empire which  
18 was so famous and so strong in Germany stated that cast  
19 iron was the nuclear power of its era.

20 In the 1800s, the late 1800s, the use of  
21 castings in the locomotive accounted for about 33 per cent  
22 of the locomotive. More recently, castings are very much  
23 used throughout the world and are very important in such  
24 items as aircraft, for the turbine blades in the engines,  
25 the canopies, the ribs in the reinforcing ribs in the wings

1 of the airplane. Dental fillings are made with castings.  
2 Prosthetic devices for use in the body are made by casting.  
3 Turbines for generating electricity are made from castings.  
4 Propellers for large steamships are made with castings. So  
5 that castings are very, very important to our daily living.

6 Q. As you look around the courtroom, Doctor Schafer, do  
7 you see any castings in this courtroom?

8 A. Well, the most spectacular casting in the courtroom  
9 is the plaque behind Your Honor's chair there which is an  
10 aluminum casting and an example of the, probably of the  
11 great casting art of the Wisconsin area.

12 There are many other castings in here. The  
13 closure mechanism over the door. Some of the supports for  
14 some of the tables, the rolling tables we have here. The  
15 support for the microphone. The magnets in both the  
16 microphones and the speakers are probably castings. Just a  
17 great number of castings around us.

18 Q. Is the art of metal casting an important one for the  
19 State of Wisconsin?

20 A. Very much so. I don't know exactly what percentage  
21 of the commerce is the casting industry here, but there are  
22 nearly a hundred foundries in Wisconsin, and it's a very  
23 important state for casting.

24 Q. Now we've used the term casting, Doctor Schafer, and  
25 in my opening statement I was referring to a casting here

1 on the table. Could you please explain to the Court using  
2 this casting and the items here on the table how a foundry  
3 would in general go about making this casting right here?

4 A. Yes. I'll come down there.

5 THE COURT: Sure.

6 THE WITNESS:

7 A. In this case the final product, which is the casting  
8 here, with a couple of pieces here that we are not  
9 particularly concerned with, is a blow chamber for blowing  
10 a core in a laboratory. The object of the casting is to  
11 make a shape that both has a dimension of desire, but is  
12 also free of defects, especially holes in the internal part  
13 of the casting. To make this casting, one uses molten  
14 metal and has to have a form or a mold in which to cast  
15 molten metal.

16 As Bruce explained earlier, the materials that  
17 we start with are simply sand -- and this is a Wedron  
18 silica sand which comes not too far from here in Illinois,  
19 and this is combined in a mixture with a fairly small  
20 amount of resin, equal portion of hardener, and a very,  
21 very small portion of catalyst, as we see here. These are  
22 mixed together and what in the foundry in the patent we  
23 call an admixture, and they are liquid or not liquid, but  
24 wet, but flowable so that they can be packed into a core  
25 box, so that the sand can be packed into the core box to

1 make one half of this particular core which forms the  
2 internal cavity in this casting. Two of these cores made  
3 in this core box are glued together to make the core that  
4 we see here. They are symmetrical, each side.

5 Using this same type of mixture, but an  
6 additional quantity of sand and resin, we prepare another  
7 admixture, and we pack this into this or over this pattern  
8 to form a mold. One side of the mold is formed in this  
9 cavity, and the other side is formed in the cavity on the  
10 opposite side.

11 The resins harden in a short period of time  
12 after they are mixed, and this time of hardening we call  
13 the strip time or the time when the mold or core can be  
14 stripped from the pattern. The time that we have between  
15 the mixing of the materials and the time when the materials  
16 must be packed in the final shape, we call this the work  
17 time or the time that we have to work with the admixture of  
18 resin, hardener, catalyst, and sand.

19 After the molds are made and removed from the  
20 patterns, we assemble the mold placing the core into the  
21 lower half of the mold which we sometimes call the drag,  
22 and then place the upper half of the mold or the cope over  
23 the core and drag producing the finished mold. At this  
24 point molten metal, and in this case aluminum, is poured  
25 into this small cavity filling the areas not occupied by

1 sand.

2           The result after cooling of the metal so that it  
3 is hard is this casting that we see here. The large  
4 section here is what we call a riser and it fills the  
5 casting with extra metal as the casting is cooling. As the  
6 metal cools it shrinks, and we would have a deformation if  
7 we did not provide extra metal to fill in the area as the  
8 metal shrinks.

9           After the casting is cooled the excess metal is  
10 cut off. By grinding we remove the flash, this material we  
11 see here, and in the final product we have this casting  
12 here which has a useful purpose, and we use these castings  
13 in our laboratory for doing test work. That is, we use  
14 this as a blow chamber for blowing sand from this cavity  
15 into a core box which now makes a what we call a dog  
16 biscuit core or a tensile core which was used to prepare  
17 some of the data that appears in these patents.

18           MR. TITTEL:

19       Q.     Doctor Schafer, is my understanding correct that the  
20 core which you stated was formed in here is the part which  
21 is responsible for the hole in the casting?

22       A.     Yes.

23       Q.     Could you give for the Court, please, Doctor Schafer,  
24 a statement of the major characteristics which are required  
25 of a core?

1 A. Yes. And if I may, I would like to list them on  
2 these sheets of paper here.

3 Q. All right. Please do.

4 MR. TITTEL: Is that okay with Your Honor?

5 THE COURT: Certainly.

6 THE WITNESS:

7 A. One of the first requirements of the core binder is  
8 it must be stable. You must be able to store it so that  
9 the foundry has time to use it. So the materials must be  
10 stable.

11 A next requirement of the binder materials is  
12 that they must be easy to mix with the sand. Thick  
13 materials generally cannot be used, such as a molasses  
14 would be very difficult to use because it would be very  
15 difficult to mix with the sand.

16 Another requirement is that the resins be  
17 compatible with the sand. So we must have compatibility  
18 with the sand.

19 MR. TITTEL:

20 Q. Would you please explain what you mean by compatible  
21 with the sand?

22 A. Well, a good example is the use of acids to catalyze  
23 furan resins which have been previously mentioned. Acids  
24 are not compatible with all sands, so that -- because  
25 there's a chemical reaction of, the strong chemical

1 reaction between the acid and the sand. So that furan  
2 resins cannot be used with certain types of sands. They  
3 are incompatible because of the fact that the catalyst  
4 that's necessary, the acid catalyst, is not compatible with  
5 the sand. So it is an important property that the resin be  
6 compatible with the sand that is desired to be used.

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1       The next property is related to the work time, strip  
2       time, that we referred to. The resin must give  
3       adequate work time.

4       Q     What happens if it doesn't, Dr. Schafer?

5       A     Well, the foundryman then would not have time to take  
6       the mixed sand and form it into the desired shape, if  
7       it didn't have adequate work time. Now, adequate work  
8       time is one requirement but then once the core or mold  
9       is shaped the foundryman wants the resin to set up very  
10      rapidly. So, he wants a quick cure so that he can  
11      strip the core quickly from the core box. So, he wants  
12      a quick cure.

13                  Now that he has the core prepared he wants  
14      it to be strong. So that he wants the resin to impart  
15      strength  
~~strong~~ to make a strong core. Now, we also distinguish  
16      strength of the core from the surface, hardness of the  
17      core. We want the core to have a good surface hardness  
18      so that the sand grains don't abrade from the core when  
19      it is handled. So, we want the core to be abrasion  
20      resistant. If it is not abrasion resistant, the core  
21      will deform and will have a rough surface on the casting  
22      and will have an inaccurate dimension.

23                  We would also next start to think about what  
24      kind of a casting the core would make. We are now  
25      ready to put it into a mold and make a casting. We

1 want the core to have enough strength at high  
2 temperatures so that it will not deform during the  
3 casting process. And appreciate that we're casting  
4 steel, the temperature's 3000 degrees Fahrenheit.  
5 So that we need good hot strength in the core. This  
6 is a very important requirement and will be, will be  
7 very important to the foundryman. In addition to good  
8 hot strength, we are concerned on what happens to the  
9 core binder after the molten metal is poured around  
10 the core.

11 And now we're concerned about gases that  
12 will be given off as the core binder breaks down,  
13 because at these very high casting temperatures the  
14 resin will decompose into smoke, gases and smoke as  
15 if you'd put a flame to something that will burn. And  
16 now we're concerned about not having a lot of gas  
17 because we have a lot of gas, the gas will blow a  
18 hole in the metal and will get cavities in the metal.  
19 So, we're concerned about not only the -- we want a  
20 low volume of gas but in addition we have found that  
21 the quality of the gas is also important. Certain  
22 gases are harmful to the metal, especially steel.

23 And nitrogen is one of these gases that's  
24 very bad. So that we're concerned about the quality  
25 of gas. We don't want harmful gases. So, not only

1 want a low volume of gas, we want no harmful gases  
2 given off.

3 Q Incidentally, Dr. Schafer, is it desirable or undesir-  
4 able for this core binder to break down at these high  
5 temperatures and decompose?

6 A Well, it's absolutely necessary for this to break,  
7 for this binder to break down because once the casting,  
8 once the metal has cooled we want to be able to remove  
9 the core from the casting. And in order for us to  
10 remove this core from the casting, we've got to get  
11 all those sand grains to become free-flowing again.

12 So, the next thing we start thinking about  
13 is the need for having good breakdown of the resin,  
14 and now we call this just breakdown or it leads to  
15 what we call shake-out. The sand shakes out of the  
16 casting easily, but we'll just call it good breakdown.  
17 As you can see, in many of these, many cases here,  
18 we're almost asking for contradictory properties in  
19 the resin.

20 In the case of the work time -- strip time,  
21 we are asking that the resin not cure for a long period  
22 of time because we want plenty of time to work with it  
23 and form it into the shape that we desire. But then  
24 contrary to that, we want it to cure very quickly. So,  
25 that we need both the slow cure and then a quick cure.

systems. And furan resin was cured with an acid catalyst. And there was a related process which was called an air set process, which was a mixture of alkyds or an oxidized linseed oil and catalysts which, again, produced a no-bake type of binder; that is, one that cured by itself in the core box usually at room temperature.

Q Are there generally considered to be two different types of binder systems, one that requires heat and one, a no-bake which does not require heat?

A Yes. And better to define that as just heat curable binders and room temperature curable binders. Sodium silicate CO<sub>2</sub> is also a room temperature curing binder.

Q Now, focusing on the time period of about 1965, could you just describe for the Court what deficiencies, if any, there were in these various binder systems you've described?

A One of the very significant deficiencies of the cores at the time was the lack of dimensional accuracy in the core. The hot processes, because of the heating and cooling of the tooling that was involved or the core box as it was involved resulted in a non-uniform dimension of the core box, because of warpage that would occur over a period of time with heating and cooling of these metal core boxes, and a change in

3-3 4 1 A Yes. In fact, it was a personal friend of mine that  
2 suggested to me that Dr. Robbins was a person of this  
3 type, and might be available for work at Asher-Daniels-  
4 Midland. Interviewed him, recommended to management  
5 that we hire him, and subsequently made him an offer  
6 and hired him.

7 Q Are you aware of Dr. Robbins' professional background?

8 A Yes, I am.

9 Q Could you --

10 A Of course, reviewed that at the time.

11 Q And would you please explain to the Court what that  
12 background was?

13 A Well, Dr. Robbins had experience in phenolic binders  
14 for the wood industry when he worked in Washington, the  
15 state of Washington, where the wood industry is very  
16 large. I forget the name of the company that he worked  
17 for. And then subsequently he had done considerable  
18 amount of urethane research at both 3-M and McAllister  
19 College, where he was working as a professor when I  
20 hired him.

21 Q You recall the approximate time when you hired him, the  
22 year?

23 A The spring of '66, I believe, late winter, early spring  
24 of '66.

25 Q Can you explain to the Court, if you know, what Dr.

- 3-2 5
- 1           Robbins' job assignment was after he joined ADM?
- 2   A    His job was to develop new binder systems for us. And  
3           more specifically, we gave him the assignment of  
4           developing a quick curing room temperature curing binder  
5           system.
- 6   Q    All right. To whom did he report?
- 7   A    He reported directly to me.
- 8   Q    Did he report to you on a regular basis?
- 9   A    Yes, he did. We had daily contact.
- 10   Q   Can you trace for the Court in your own words, Dr.  
11           Schafer, the events which led up to the discovery  
12           Robins  
13           by Dr. Robbins of Isocure?
- 14   A    Yes. The first event of any significance perhaps was  
15           the discovery of the benzylic ether resin.
- 16   Q    That's the resin that's sometimes referred to as the  
17           Pep resin?
- 18   A    Yes. I don't know exactly the details that led up to  
19           the discovery of this resin, but I remember that Janis  
20           Robins  
21           Robbins one day came to me and said I have this new  
22           resin. And he described it.
- 23   Q    What was it?
- 24   A    And --
- 25   Q    What was your reaction to that?
- 26   A    Well, my reaction was, this is very nice and it does  
27           seem to me to be completely new. But at the time I

3 6  
1 really didn't know what we were going to do with it.  
2 Since we had no way to use it at that time to make a  
3 core. I remember we discussed that Janis felt that  
4 resin would be more reactive than other phenolic resins  
5 of a similar nature but different. And he said, well,  
6 maybe we can make a no-bake binder out of it or maybe  
7 we can make a hot box binder out of it using acid  
8 catalysts since it should cure a little more rapidly.  
9 But then he tried these and found no significant  
10 difference or improvement in making cores compared to  
11 the previous art. So, we kind of said, well, very  
12 nice, but go back and discover something we can use.

13 THE COURT: This might be a good point to  
14 call it a day. We will generally have our starting  
15 time be determined by what else I have on my calendar  
16 in the morning, and I'd suggest tomorrow morning we  
17 start at 9:45. Agreeable?

18 MR. TITTEL: That's fine, Your Honor.

19 MR. EGAN: That's fine.

20 THE COURT: We'll be in recess then until  
21 9:45.

22 (Proceedings concluded at 5:15 p.m.)  
23  
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25

1           temperature binder system after the discovery of  
2           Pep resin?

3       A    Well, as I was just finishing up yesterday, the  
4           benzylic ether resin, because of its composition, was  
5           thought to be especially reactive as a phenolic resin.  
6           And we tried it as a hot box binder and as a shell  
7           resin binder, and even as a no-bake binder, using  
8           acid catalysts to cure the resin.

9                          In the case of the hot box and the no-bake,  
10                  and used hexamethylenediamine and formaldehyde as  
11                  crosslinking agents for the shell process.

12                          This special resin, in spite of our  
13                  expectations, did not perform unusually in any of  
14                  these applications when compared to conventional  
15                  phenolic resins.

16                          As a result, we, or I said to Janis at the  
17                  time that this was interesting, but we needed something  
18                  that would be truly fast and truly room temperature  
19                  curing. I'm not sure what happened in Janis' mind,  
20                  but I know he then started searching for something  
21                  beyond this.

22                          At some later period, I believe a couple of  
23                  months later, Janis came to me one day and said, Come  
24                  on, I've got something to show you.

25                          And he took me out into the laboratory and

1 demonstrated the gas cure process, which came to be  
2 known as the cold box process and sometimes as the  
3 Isocure process.

4 Q Well, what was your reaction when you saw that system?

5 A I was immediately impressed. In fact, I remembered  
6 particularly that the strength of the cores produced  
7 almost immediately upon gassing at room temperature  
8 were outstanding, the range of 100 PSI or something  
9 like that. And for a first experiment, this was, I  
10 felt, just really excellent.

11 And it seemed to have all the characteristics  
12 that would be needed in a good foundry binder, as far  
13 as we were able to see from our core-making work.

14 We immediately started to make plans for  
15 doing evaluations in our pilot's foundry, which we  
16 had right at the laboratory, to determine whether it  
17 would have good gassing properties.

18 Very shortly thereafter, a few days, we  
19 made up some cores that could be tested in the foundry.  
20 And, again, the results were quite encouraging. So,  
21 I was extremely impressed.

22 Q What is your reaction today to that development?

23 A Well, it speaks for itself almost. It's been one of  
24 the most outstanding discoveries in the history of  
25 core making in the foundry industry. It's really

1                   Theim Products here in Milwaukee.

2                   Then there were other binder systems that ADM  
3                   did not manufacture, the shell resin systems, which  
4                   were dominated by the ~~Beebe~~ <sup>Durez</sup> Division, which is now  
5                   part of Hooker; Monsanto; Borden, Reichtholt.

6                   I think I hit most of them. I may have missed  
7                   a few.

8                 Q In 1956 could you kind of generally describe for the  
9                   Court what the state of the foundry binder art was in  
10                  terms of the various classes, if that's a proper word,  
11                  of the binder systems available?

12                A There were three major binder systems used in the core  
13                  room. There was the core oil system, which was described  
14                  before, which was a baking system. The shell resin  
15                  system, which was part of the war spoils from the war  
16                  coming over from Germany, which by that time had had  
17                  significant acceptance in the industry. And the CO<sub>2</sub>  
18                  process, again, which came over from Germany, and had  
19                  some acceptance. It was something new.

20                   And then starting just in 1955, '6 was a new  
21                  concept which was called an oxygen-setting oil, which  
22                  was a sort of a no-bake type product.

23                 Q Did ADM in that time period perceive a need for  
24                  improving upon these binder systems?

25                 A Yes, they did. It was the reason I was moved into the

1           of new products management. There had been old manage-  
2        ment in the division, and they let the product line  
3        decline. So, my first job was to try to develop  
4        products which would equal some of the newer systems.

5           We looked at the sodium silicate CO<sub>2</sub> system  
6        and brought out a, our first line of binders to compete  
7        in this field.

8           We brought out an oxygen-setting oil to  
9        compete in that field. It was a new concept. And we  
10      made several attempts to develop shell resins, and we  
11      were not successful to really getting that moving and  
12      get it into the marketplace.

13     Q    What were they — excuse me.

14     A    Okay.

15     Q    What were the major qualities of the prior art binder  
16      systems which needed improvement upon?

17     A    Well, everybody at that time was looking for systems  
18      that first were faster, that gave better dimensional  
19      tolerance to the mold or the core, and those that could  
20      be used without heat.

21           There was a move toward eliminating heat from  
22      the core room and the molding concept.

23           An additional quality that they were looking  
24      for was surface finish. And this comes, of course, from  
25      the core or the mold. And, so, they are looking for

1 ways to improve the surface finish of the castings  
2 through better bonding mechanisms.

3 Q Were these needs to improve generally known in the  
4 industry?

5 A I think they're pretty well known. Like most industries,  
6 the needs actually were identified by the customer.

7 We had continual meetings with our key  
8 customers. I guess you call them sort of rap sessions,  
9 talking about where we were at and where the industry  
10 wanted to go. We had meetings with Ford and General  
11 Motors and with International Harvester, and some with  
12 Deere, John Deere. And our ideas, really, came from  
13 our customers.

14 Q What steps, if any, were taken towards developing new  
15 binders to satisfy these needs?

16 A Well, through our discussions with the customers, we  
17 first tried to get it down on a piece of paper so we  
18 could understand. And we developed a list of objectives  
19 that we felt that the binder systems of tomorrow should  
20 have. We then saw that -- and this is in a time frame  
21 of the late fifties -- that we really didn't have the  
22 manpower from a technical standpoint to accomplish the  
23 job.

24 Now, we had to make a decision on whether we  
25 wanted to take and risk the investment of additional

1 personnel in the area of research and technical  
2 development to try and develop these processes.

3 Q Were any steps taken towards budgeting money for  
4 research?

5 A In 1963 we, as a management, a young management group  
6 at that time because we were all quite young, put  
7 together a program of what we thought we could do and  
8 why we thought we could do it and the amount of money  
9 it would cost.

10 And we presented it at that time to the board  
11 level of Asher-Daniels-Midland in order to get a commit-  
12 ment from them, because it was a long-term program; it  
13 wasn't something where we could invest money today and  
14 get an immediate return on it tomorrow.

15 So, we had to get an understanding and an  
16 agreement from the management of ADM, which we did.  
17 And we agreed that we would budget a substantial amount  
18 of money in the research and development effort, and  
19 with the objective of building what we have today.

20 Q And as a result of this increased research by it, was  
21 research conducted in the area of trying to develop a  
22 new binder system?

23 A Yes. The first thing we had to do after we got a  
24 commitment on the money, which virtually increased our  
25 expenditures threefold from where we were at at that

1 time up to a level of about five percent on sales, which  
2 was practically our total profit, we went out and  
3 secured somebody to run the program because we had  
4 nobody internally that we felt had the technical skills  
5 to run it. And that is when we brought Dr. Schafer on  
6 the scene.

7 Q Okay. Can you describe generally for the Court some  
8 of the systems that you worked with prior to the time  
9 Dr. Robins discovered Isocure?

10 A Our first systems were in the area of furfuryl alcohol  
11 binders, which was an improvement, we felt, over the  
12 oxygen-setting oils. We brought those into the market-  
13 place. That was actually prior to this time, which  
14 actually showed little success.

15 And the first major one was our development  
16 of Linocure, which has been discussed today, which was  
17 an alternative no-bake.

18 Then we found that these systems did not have  
19 the high speed that the industry, the production part  
20 of the industry, the high productivity foundries like  
21 the automotive and farm implement -- we didn't satisfy  
22 those needs. We tried several things.

23 We tried what we called an ABC process which  
24 was a high-speed furan process coupled with high-speed  
25 mechanical handling equipment. We actually presented

1           this to several people, including Ford Motor Company,  
2           and had considerable work together with their manufac-  
3           turing research and development, trying to adapt this  
4           principle and concept to the foundry industry.

5           We found that it was not practicable. We  
6           came out with the solvent evaporation process which  
7           fundamentally was putting a binder and solvent in the  
8           sand and then blowing the binder off the sand and having  
9           it solidify. We had problems with this because it was  
10          too slow. We didn't get good, strong cores.

11          We had another system, which again was based  
12          on acid curing materials. We tried to use them with  
13          such things as chlorine and boron trifluoride. We  
14          found that it worked.

15          We actually presented it at the convention  
16          back in the, I guess, the early sixties. But the  
17          problem was the gases were so toxic that it really  
18          wasn't practicable to handle them in a foundry  
19          environment. So, we had quite a few system failures  
20          before we came out with our products that are under  
21          discussion today.

22          Q     Do you recall, Mr. Dorfmüller, the first time that  
23           you ever saw the Isocure system?

24          A     Yeah.

25          Q     Could you please describe for the Court what you remember

1 and what your reaction was?

2 A It sure happened shortly after I was married, and it  
3 was in the fall of '65. And I was called up to see  
4 this new system; it didn't have a name at that time.  
5 And Dr. Schafer and Dr. Robins demonstrated what we  
6 now call Isocure.

7 And I was just utterly amazed because it was  
8 fast, it was almost instantaneous, and the resulting  
9 cores with sand was extremely hard with very good  
10 surfaces. And I was just excited like the devil.

11 I didn't know if the economics were any  
12 good, and I didn't know if we could make good castings,  
13 but I had no doubt we could make good cores and molds.

14 I called up my wife and told her that if  
15 this thing was as good as it looked, it looked like  
16 our career was carved out, and I didn't have to worry  
17 until I was 60 years old.

18 THE COURT: It's a nice feeling, isn't it?

19 THE WITNESS: Yeah, particularly with a new  
20 wife.

21 MR. TITTEL:

22 Q Did Dr. Robins' efforts result in any other binder  
23 system?

24 A It resulted in the binder system we now identify as  
25 Pep Set.

1 gross profit, going up to 4.4, and proceeding very  
2 rapidly in the middle 1970s until 1979 it amounts to  
3 61.3 percent of the total profitability of the division.

4 The next column shows the development and  
5 research expenses of the division, starting at \$445,000  
6 going up to \$1,800,000 over the course of time. The  
7 phenolic urethane portion of the research expense is  
8 noted below.. And it shows below that the very bottom  
9 line is the cumulation, which is the sum of the years  
10 before up to date.

11 I think the significant thing here is to  
12 see that by 1973 we had \$710,000 invested in phenolic  
13 urethane research and development, and it was up until  
14 our cumulative profits from the Isocure and the Pep Set  
15 gross profit level.

16 Remember, that's before we got any, before  
17 we deducted our sales costs. So, it's not a true  
18 reflection. But it took us five, six years to recover  
19 our research investment and get on a profit side, even  
20 at the gross profit level.

21 Q Did you recommend to senior management that these sums  
22 be expended?

23 A I did.

24 Q Would you have done that, Mr. Dorfmueler, if it would  
25 not have been possible to obtain patents?

1 manager of the division and about a year later  
2 vice-president.

3 Q. Have you during this period of time had any  
4 opportunities to visit foundries?

5 A. Yes. I have visited a great number of foundries,  
6 not only in the United States but in various parts of the  
7 world. In fact, during the middle Sixties I did quite a  
8 bit of foreign travel and work in setting up our new  
9 operations in such countries as India and South America and  
10 France. So I suspect I've visited at least in excess of a  
11 hundred foundries.

12 Q. Have you had opportunities to visit foundries in the  
13 mid-Sixties?

14 A. Yes.

15 Q. How would you characterize the importance of the  
16 foundry industry to the United States?

17 A. Well, the foundry industry is made up of about 4400  
18 foundries at the present time. It is the fifth largest  
19 industry in the United States in terms of value added by  
20 manufacturing, and in 1979 approximately 20 1/2 million  
21 tons of castings was produced by this industry. And of  
22 course as has been mentioned earlier in testimony these  
23 castings are used by every one of us in all walks of life.  
24 They are very important to us.

25 Q. Do you recall when Isocure was introduced by Ashland?

1 amine gas, and there was certainly no provision for doing  
2 that in the old equipment. They had generally to consider  
3 the faster curing properties of the cold box. So the cycle  
4 time in the machining had to be speeded up to take  
5 advantage of it, and so the equipment people at that time  
6 recognized that we had something here and they did get into  
7 the act early in the game to try to develop equipment  
8 specifically adapted to the cold box process and that, of  
9 course, they realized I'm sure early on that there was some  
10 risk involved, but they were willing to take that or make  
11 that investment to convert existing technology and  
12 equipment or to develop new machines for this purpose.

13 Q. Who were the equipment people that you worked with?

14 A. Well, we worked with the Shellco Company in  
15 Cleveland, Ohio, Beardsley & Piper Division of Pettibone in  
16 Chicago, and Sutter Equipment Company, that's S-u-t-t-e-r,  
17 located up in Michigan.

18 Q. At the time you were introducing Isocure, if you had  
19 walked in to a foundry to try to sell them this product,  
20 what would an exemplary foundry have had to be persuaded to  
21 do in order to get into the Isocure system?

22 A. Well, the higher production foundries were in a  
23 position of having just invested, say, 7 to 8 years earlier  
24 in the fastest production equipment at the time, which was  
25 hot box and/or shell equipment, and so they had

1 considerable investment involved in this process, and it  
2 was certainly with some reluctance on their part that they  
3 wanted to turn around and put that investment aside and  
4 reinvest in new equipment to use the cold box process. So  
5 they had to be convinced that this was indeed a  
6 revolutionary advancement in the art and that it was worth  
7 their while to make this kind of move, and as was evidenced  
8 in the growth rate of Isocure in the earlier years it was  
9 quite obvious that this was a difficult step for them to  
10 make and a difficult decision for them to make.

11 Q. Referring to the hot box machine that you've  
12 described, what sorts of modifications would have to have  
13 been made specifically to it? Any added equipment, any  
14 changes in the equipment itself in order for the adaptation  
15 of it to Isocure?

16 A. Well, the primary change had to be in the removal of  
17 the heating mechanism and the introduction of some manner  
18 for injecting the gas into the system, into the pattern  
19 after the sand had been blown into it, and to find some way  
20 to contain that gas so that it would not leak into the  
21 atmosphere and to collect it and scrub it afterwards. So  
22 that there were several changes that had to be made and the  
23 cycling of the machine had to be set up in such a way as to  
24 take advantage of the fact that you could blow the sand and  
25 cure it within a matter of seconds and eject that cured

1 core and then go into the same cycle over again.

2 Q. Has Isocure been sold to foundries that did not have  
3 the hot box equipment?

4 A. Yes. Some smaller foundries were able to adapt very  
5 simple core oil type blowing equipment and using a manually  
6 movable gas manifold gas these cores and get into the  
7 business with rather small investment. But these were  
8 generally small shops with lesser production requirements.

9 Q. Well, how did you go about persuading these  
10 foundries to undertake all of this change in equipment to  
11 go into Isocure?

12 A. Well, it was quite a job to get to the right people  
13 in the larger foundries. It involved a top management  
14 decision to invest this money that was necessary to convert  
15 to the Ashland process using Isocure. So the whole system  
16 of selling had to change in that earlier we would expect a  
17 salesman to go in with a common line of products and talk  
18 to the foundry manager, core room superintendent, the core  
19 room foreman, and get a test or help him with whatever  
20 problems he had in introducing our product as opposed to  
21 somebody else. But here was a case where talking to those  
22 people was of no help to us. We had to go to the top  
23 management and convince them that this was a cost saving  
24 device and that they were going to have to spend X dollars  
25 to put this equipment into use, but that it would have a

1 payout, and that was the means and the method that we used  
2 over a period of time to convince the large foundries to  
3 make these conversions.

4 Q. When you say this was a cost saving system, in what  
5 respects?

6 A. Well, in several ways. First of all, you have to  
7 appreciate that the productivity is much higher, which  
8 means that a given machine can turn out more cores per hour  
9 of the same size as you would get with, say, a hot box  
10 operation. The fact that you have to use fewer machines  
11 means that the labor requirement also is less. You have  
12 fewer people operating these machines.

13 You have, actually if you're starting a new  
14 operation you have less floor space involved, less space  
15 involved in setting up this whole operation.

16 You have a large saving in the fact that because  
17 you're not operating with a heat cured system the pattern  
18 equipment into which the sand is blown is not subjected to  
19 the multiple heating and cooling cycles which tend to  
20 produce wear and distortion in the metal patterns and  
21 inaccuracy. So you don't have to replace those so often.  
22 In fact, that's probably the largest single savings that a  
23 foundry can enjoy when they convert from one system to the  
24 other.

25 And so as a result of all of these savings — we

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1           illustrating the consumption of binder, Isocure and  
2           Pep Set binder in the United States and foreign  
3           countries?

4       A   Yes, if you look at the total worldwide consumption,  
5           we had some numbers earlier just showing the domestic  
6           consumption or sales of Isocure and Pep Set. More  
7           than 50 percent of the total of these binders used in  
8           the world are used outside of the United States. And  
9           if you total up all of the pounds that were sold in  
10          the foundries around the world in 1979 and you calculate  
11          the amount of sand which, foundry sand which would be  
12          coated by that amount of resin in the world at 1 and 1/2  
13          percent a binder, it would fill over 16,000 boxcars,  
14          which would make up a train 168 miles long, or from  
15          Milwaukee to Sturgeon Bay, approximately.

16      Q   Mr. Sparks, have any tributes been paid to Isocure and  
17           Pep Set by the foundry industry?

18      A   Yes, a number of them have been made, and probably  
19           those which are most visible are various articles  
20           which have been written by foundrymen published in  
21           the Modern Castings magazine and the Foundry magazine,  
22           which are the two national foundry magazines. There  
23           are a large number of these which have been published  
24           over the past 10 to 12 years since the introduction  
25           of Isocure. There are and have been worldwide a number

1 of seminars presented and talks given about this  
2 process at local American Foundrymen's Society chapters  
3 and other foundrymen's chapters around the world.

4 I think one of the very strong examples of  
5 honors given would be the Joseph S. Seaman Gold Medal  
6 Award, which is one of the most prestigious awards  
7 granted by the American Foundrymen's Society to  
8 individuals of merit within the industry. Now, this  
9 award was presented in 1970 at the American Foundrymen's  
10 Convention in Cleveland to Tony Dorfmüller, as I  
11 remember the approximate wording, for support of the  
12 research and development and application of new core  
13 binder technology to advance the cast metals industry.

14 Q Now, this is the Tony Dorfmüller who testified?

15 A That is correct, yes.

16 Q Now, I will hand you Exhibits 82, 83, 85, and 87 to  
17 105, as well as Exhibits 184 to 194, and ask you if  
18 you will identify them?

19 A Yes, this is a grouping of exhibits which are reproduc-  
20 tions of articles, papers, which have been presented  
21 at casting congresses, and these have been authored  
22 by various people in the industry, and both domestically  
23 and internationally. And these would have appeared in  
24 the Modern Castings magazine or Foundry magazine, and  
25 some of them will be found in the transactions of the

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1 A Okay. Is that all right?

2 Q I think that's fine.

3 What's the size of Universal Foundry in terms  
4 of number of employees, how much metal the foundry  
5 pours?

6 A In better business days, 500 hourly employees, 100  
7 salaried employees including myself, with 150 tons of  
8 gray iron, 25 tons of ~~ductile~~, and 10 tons of aluminum  
9 poured daily.

10 Q Now, you mentioned that Universal Foundry was involved  
11 in complex castings.

12 Will you elucidate for the Court what you  
13 mean by that?

14 A Complex casting is a casting that requires, in my  
15 opinion, several cores. Now, an average casting has  
16 three cores in it. And we have some castings that  
17 require as many as 27.

18 Q How many cores a day do you make at Universal Foundry?

19 A Between 12,000 and 14,000 a day.

20 Q Can you trace now for us your background and experience  
21 in the foundry industry?

22 First, how long have you been in the foundry  
23 industry?

24 A Nineteen years.

25 Q All right. Can you start chronologically and bring us

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1 to include core-making, with the addition of three  
2 additional machines and two mixers. It's a quarter of  
3 a million dollar operation just for the equipment.

4 Q Prior to installing Isocure, how long did it take you  
5 to make the shell?

6 A The shell for an air-cool cylinder, depending on the  
7 size of the engine and whether it was a single cylinder  
8 or twin, took between four and a quarter minutes to  
9 five minutes thirty seconds, about five and a half  
10 minutes.

11 Q Now, after you installed Isocure, how long did it take  
12 to make that?

13 A I'm very proud of this unit. We now make air-cooled  
14 cylinder molds in 56 seconds, both halves of the mold,  
15 the cope and the drag.

16 Q Both halves of the mold at one time?

17 A Yes, sir.

18 Q In 56 seconds?

19 A Yes, sir.

20 Q Can you describe for us now your Pep Set application?

21 A In 19, very early in 1975 we had a mixer that was  
22 purchased prior to my employment at Universal, and it  
23 was just sitting in the box. Nobody even knew what to  
24 do with it.

25 I had had prior experience with Pep Set.

1 I contacted Ashland and said, Send me a couple of  
2 barrels. And we started making some cores.

3 At Universal we have some very exceptional  
4 foundry people, but they didn't believe me when I told  
5 them we could make jacket cores out of something other  
6 than oil sand or shells. And it was rather an interest-  
7 ing experiment, not only from the standpoint of making  
8 the cores, but for getting people who didn't know me  
9 very well to appreciate that I knew what I was talking  
10 about.

11 Q And how did that test come out?

12 A Super. We have since installed a 500 pound a minute  
13 mixer, a sand reclamation system, bulk resin tanks.  
14 We spent well over \$400,000 just on our Pep Set units.

15 Q What size molds are you making now in Pep Set?

16 A The average molds would be 150 pounds.

17 Q And how many molds did you make, say, in oil sand before  
18 you switched to Pep Set on a daily basis?

19 A 200 to 220.

20 Q How many did you make after you switched to Pep Set?

21 A Between 500 and 540.

22 Q And how long did it take you to make the molds before  
23 you switched to Pep Set?

24 A In oil sand, because of the lack of grain strength, it  
25 was required that we use what we call a hairpin. It's

1           a small wire that helps support the sand till it's  
2         baked. And a three-minute cycle was a good cycle.  
3         And the same mold with the same tooling we put it in,  
4         on the Pep Set line, and we were stripping 150 pounds  
5         of sand in 52 seconds.

6       Q    Can you describe now for us what savings you realized  
7         by employing the Isocure and Pep Set systems at  
8         Universal Foundry?

9       A    The most significant savings, and my accounting people  
10      would point out, would be we in today's prices, we  
11      save better than \$40,000 a year just in natural gas.

12           In '77 a therm or 100,000 BTU gas was 19  
13      cents. Today it's 32 cents. And more than likely,  
14      before the end of next year, it will be 40 cents a  
15      therm.

16           By eliminating to a great extent that  
17      production that required heat, that was the single  
18      savings of \$40,000 a year. The other savings that  
19      are more important to me, I have a casting that I  
20      don't have to spend as much time in the cleaning room,  
21      preparing it for shipment as I did in oil sand. And I  
22      can use as cheap a tooling in Pep Set as I could in  
23      oil sand, and certainly far less expensive tooling than  
24      required for heat processes.

25       Q    All right. With regard to the savings in natural gas,

1 can you describe for us what pieces of equipment and  
2 what processes you were able to eliminate by employing  
3 Isocure and Pep Set?

4 A We'll take Pep Set first.

5 Q Fine.

6 A In Pep Set we used a verticle tower. The requirement  
7 of that burner is 1,750,000 BTU an hour. That's 17  
8 and one half therms of gas. That was the biggest  
9 single elimination of natural gas.

10 In Isocure, our 4103, that's the core machine,  
11 replaced four U-180's; and nominal comsumption on the  
12 U-180's, and I have a lot of them, is a therm of gas  
13 an hour.

14 Q Now, what processes were you using of U-180's in?

15 A Shell.

16 Q Shell. Okay.

17 A The 4103 took the place of four U-180's. And the three  
18 Isocure machines, my industrial engineering department --  
19 and I have a large industrial engineering department --  
20 tells me that each Isocure machine replaces two and  
21 three-quarter shell machines.

22 So, it's, I haven't done my arithmetic,  
23 three times 2.75.

24 Q All right. Very good. Has the employment of Ashland's  
25 Isocure and Pep Set processes at Universal Foundry

1                   increased the productivity of your foundry?

2       A    Oh, very definitely. I just say, one Isocure machine  
3                   replaced 2.75 shell machines.

4       Q    All right. With regard to these processes, what are  
5                   the primary benefits you see from their use? What do  
6                   they do for you?

7       A    Well, one thing, my employees don't have to handle hot  
8                   molds and cores. When they made molds and baked sand,  
9                   they were handling a mold that weighed 150 pounds, 75  
10                  pounds a half. And it would come out of the verticle  
11                  oven in the neighborhood of 300 degrees.

12                   They like the fact that they don't have to  
13                  handle hot molds and cores. But more importantly, to  
14                  me, is I have absolutely producibility of the tooling.

15                   In my pattern division bills the tooling  
16                  property in two dimision, then I know that my cores  
17                  or my molds are going to positively duplicate because  
18                  we cure in the pattern in the core box, and that's one  
19                  of the things I like about the process.

20       Q    Okay. Can you tell some of the things you like about  
21                  the process?

22       A    Cost. Costs, not only from a standpoint of price per  
23                  pound of prepared sand -- the shell sand that I use,  
24                  and I use, still use an awful lot of it, is six cents  
25                  a pound at the machine. That's what we use in our

1 development of our costs.

2           Pep Set and Isocure is closer to 2.15, 2.2  
3 cents a pound. Now, I do have to, I use a factor of  
4 40 percent. If I have been making a core and shell  
5 and I change it to Isocure, I have instructed my  
6 estimating department to take the weight of the shell  
7 core, add 40 percent to it, and then apply the cost  
8 of the sand to that.

9           So, we might get out at about three, a little  
10 over three cents a pound.

11 O We've talked about the speed of the processes. Does  
12 that have practical, beneficial results at Universal  
13 Foundry?

14 A It's been extremely helpful most recently. One of my  
15 considerations initially in employing both processes  
16 was speed. But just last week a customer who ran out  
17 of inventory and he had to have 5,000 castings in ten  
18 days. It was almost laughable. But with Isocure we  
19 were able to produce the cores. You got to make the  
20 cores before you make the castings.

21           In shell, we had something less than a four-  
22 minute cycle on the particular core for the pump housing.  
23 And in Isocure it's less than a minute. So, we were  
24 able to meet the requirements. We would not have been  
25 able to meet the requirements without it.

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1 reused. I find that the phenolic urethane system,  
2 because of the high tensile strength with relatively  
3 low binder levels, is very easy to reclaim.  
4

5 I operate with less than one half of one  
6 percent retained sand on the reclaimed sand, is a  
7 measurement we use.

8 Q Based on your knowledge and experience over the past  
9 19 years in core-making, mold-making processes and the  
10 binder systems available, in the mid to late 1960s, was  
11 there a need for a breakthrough in sand binder  
12 technology?

13 A I believe that there was. We'd had some good technolog-  
14 ical breakthroughs right after the Second World War and  
15 up through the 1960s. Most of the core-making technology  
16 had been centered around hot processes.

17 With the introduction in the very late 1960s  
18 of a cold process that was rapid, it got the attention  
19 of the foundrymen.

20 Q Did Ashland's Isocure and Per Set system provide the  
21 foundrymen with this breakthrough?

22 A Yes, it did.

23 MR. CHAMBERS: Thank you, Mr. Cartwright.  
24 Thank you, Your Honor.

25 BY MR. BRYAN: ~~CROSS EXAMINATION~~

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1 MR. CHAMBERS: The next witness is Mr.  
2 Leo LeBlanc.

3 THE COURT: Raise your right hand, please.

4 (Witness sworn.)

5 THE COURT: Be seated, please. State your  
6 name and spell your last name for us.

7 THE WITNESS: All right. My name is Leo  
8 Joseph LeBlanc. I live at 3837 Shellmore Avenue,  
9 Brookfield Hills, Michigan.

10 LEO J. LEBLANC, called as a witness on  
11 behalf of the Plaintiff, being first duly sworn on  
12 oath, testified as follows:

13 DIRECT EXAMINATION

14 BY MR. CHAMBERS:

15 Q By whom are you employed, Mr. LeBlanc?

16 A I own my own company in Muskegon, Michigan, which is  
17 a foundry and machine shop making castings for the  
18 petroleum equipment industry, employing about 120  
19 people, and doing about \$10 million a year in sales.

20 Q What's the name of your company?

21 A Enterprise Works.

22 Q Can you give us your education above the high school  
23 level?

24 A I graduated from Queens University in Canada in 1949  
25 with a degree in mechanical engineering. And after

1           that I went to Harvard Business School and got a,  
2           more equivalent to an associate degree called TMD,  
3           which is a poor man's MBA.

4       Q    Can you trace now for us your work experience?

5       A    Yes. I started in the foundry industry in Canada, a  
6           company called Amperes Imperial, and helped develop  
7           a centrifugal casting process there.

8                   And I was then hired after four years by  
9           Woodward Company out of their pipe division to mechanize  
10          their plant. And I was with them 1954. I started as  
11          chief engineer and rose up to vice-president of  
12          operations through 1970. And we grew from about --

13       Q    Stopping there for a moment. How many plants did  
14          Woodward Iron Company have that you are responsible  
15          for?

16       A    I was over about ten different foundries, employing  
17          about 8,000, 9,000 people. And in 1969 we got purchased  
18          by Mead Paper Company. And as I said, we had grown  
19          from about \$50 million, \$60 million, up to \$700 million.

20                   And I saw that after we were purchased that  
21          their goal was to get us back to the \$70 million, and I  
22          left the company.

23       Q    And what was your next position then?

24       A    I then went as vice-president of Kelsey-Hayes Foundries  
25          in Detroit, Michigan. I was over two plants, one in



1 converted a plant in Chatanooga, Tennessee, and  
2 installed Isocure core machines and converted their  
3 machine into a molding line for automotive and truck  
4 industry. And, also, their steel foundry in Atchison,  
5 Kansas. We drew it and put it in a, I think, one of  
6 the most automated no-bake lines in the country, making  
7 axle hoses.

8 Q And then what was your next position?

9 A Then I bought my own business and went into business  
10 for myself, and I've been doing that for three years.

11 Q Are you familiar with Ashland Isocure and Pep Set  
12 systems?

13 A Yes, I am.

14 Q Had you been responsible for installing any of, either  
15 of those systems in any of the places where you've  
16 worked?

17 A Yes. I first got interested in Isocure in, oh, early  
18 '68. And I had visited at that time, I think, the first  
19 installation was a ~~four-city~~ <sup>Forest City</sup> installation in Cleveland.  
20 And I think we were making valve bodies for, I think,  
21 Vickers.

22 And they were using shell. And at this time  
23 Isocure was just in its infancy, and I was quite  
24 impressed by their results.

25 Q What impressed you about their results?

1 A Well, the core was a very, or the casting was a very  
2 complex casting. It had to be 100 percent pressure  
3 tight, and the shell core that they used, apparently,  
4 was involving a lot of gas during solidification and  
5 was causing problems in the casting period in the  
6 conversion of Isocure, which rapidly went from 35  
7 percent down to about five percent, and that impressed  
8 me very much.

9 And shortly thereafter signed the secrecy  
10 agreement with Ashland, and we were on a project of  
11 putting them in the different divisions of Woodward  
12 when Mead Paper Company took us over.

13 Q All right. Now, when you went to Kelsey-Hayes, did  
14 you employ the Isocure process there?

15 A Yes, we used the Isocure process. In fact, I think,  
16 if memory serves me right, we were one of the first  
17 highly automated companies to use Isocure.

18 We made rotor cores that was previously  
19 made in shell.

20 Q What was your involvement with installing that system?

21 A Well, my involvement, when I came with Kelsey they  
22 were just starting up. My involvement was to get it  
23 working and make sure it worked because we had burned  
24 our bridges behind us, and we had technological  
25 difficulties as you start up, as you did with any new

1 process. And shortly thereafter it was very successful.

2 We made, oh, an average of 800, 900 cores an  
3 hour, and then we converted our Freemont from sand to  
4 oil core to Isocure and for a casting for molds that  
5 went over a rotor.

6 Q Can you estimate for us roughly in dollars how much  
7 equipment you've installed in the various places to  
8 practice the Isocure - Pep Set process?

9 A In Kelsey-Hayes it was somewhere in the neighborhood  
10 of slightly under \$1 million. Chatanooga, Tennessee,  
11 the core room there cost us around \$3 million or \$4  
12 million. The Atchison no-bake axle line complete was  
13 about \$3 million.

14 Q And what process was practiced at Atchison, Isocure or  
15 Pep Set?

16 A That was the Pep Set.

17 Q Why did you choose to employ Isocure and Pep Set at  
18 these various locations?

19 A Well, basically, all things considered, it reduced  
20 the cost of our finished casting. That was the main  
21 reason.

22 Q Can you explain for us how it reduced the costs?

23 A Well, in oil sand, we'd have to go -- what you replace  
24 in oil sand, the handling, the breakage, the lack of  
25 dimensional stability, which increased scrap rates

1           not only in your core room but in your finished castings.

2           The no-bake Isocure process eliminated most  
3           of this, and you got a better finish and less scrap  
4           in your castings. And the resulting core cost was  
5           cheaper.

6       Q   Did you receive any other benefits that you can think  
7           of?

8       A   Well, yes. On Isocure you did get a better finish  
9           versus oil sand, less burn in, better dimensional  
10          stability.

11      Q   Now, you've been in the foundry industry for how many  
12          years?

13      A   All my life. I've often wondered what I did wrong.

14      Q   Based on your experience in the foundry industry and  
15          your knowledge of core-making or mold-making processes,  
16          in the mid to late 1960s was there a need for a foundry  
17          sand binder breakthrough?

18      A   Yeah, there definitely was a need for a better core.  
19          The foundry industry, ironically, as those here in the  
20          room can tell you, up to that time there's millions of  
21          dollars spent on research making the mold cheaper; not  
22          a whole lot on making the core cheaper.

23           Your Honor, it cost us as much to make the  
24          inside of the casting as the outside. There was very  
25          little done to reduce the cost of the process, other

1 than what was brought in this country from Germany  
2 after the War Reclamation Act, and the process was  
3 around even longer than I was.

4 Q Did Ashland's Isocure and Pep Set provide the foundry  
5 industry with this breakthrough?

6 A Yes, it did.

7 MR. CHAMBERS: Thank you, Your Honor.

8 CROSS EXAMINATION

9 BY MR. EGAN:

10 Q Mr. LeBlanc, does your foundry use binders in addition  
11 to Pep Set and Isocure?

12 A The foundry I have now?

13 Q Yes.

14 A Yes, we use, we use shell, CO<sub>2</sub>, and I'm putting in a  
15 Pep Set line right now. And we operate within about  
16 four weeks, I hope.

17 It does not use — when I bought the foundry,  
18 there was no no-bake used at that plant.

19 Q No no-bake at all?

20 A None whatsoever.

21 Q And in the foundries in which you had a hand in installing  
22 Pep Set lines or Isocure lines, did that completely  
23 wipe out the use of other binders?

24 A Generally speaking, we replaced, at Kelsey-Hayes,  
25 completely replaced the oil sand cores, and both at

1 Detroit and Freemont. And, of course, the installation  
2 at Chatanooga replaced -- there was no, it was a new  
3 installation, so, it didn't replace anything. It was  
4 a new installation.

5 And at Atchison, we replaced green sand  
6 molding with the Pep Set. And the interesting thing  
7 in a steel foundry, you go and ask what scrap they run,  
8 they say they run one percent, but they weld it in the  
9 cleaning room. And the irony was, at Atchison was the  
10 pounds per ton, and it was used in the steel industry.

11 When you put in the, before we put in the  
12 new no-bake Pep Set line, they were running about 40  
13 pounds a ton.

14 Q Of scrap?

15 A No, 40 pounds of welding rod per ton of casting. And  
16 after we installed the no-bake, that dropped to about  
17 ten, which saved roughly about \$10 million a year.

18 Q Have you ever had any experience with Delta's Quick Set?

19 A Very little, but some.

20 Q What do you know of that?

21 A Well, forgetting -- Jim, when I was at Muskegon, I can't  
22 think of his last name, worked for Delta, tried some  
23 tests on it. And my memory's aged. I know it didn't  
24 replace it. I really -- it's so hazy, I can't remember.  
25 It's back so many years. But that's the only time I

**Page Missing from  
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November 5, 1968

Janis Robins

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 1, "100%" should read -- 10 $\frac{1}{2}$  --. Columns 9 and 10, TABLE III, third column, line 8 thereof, "6.8+" should read -- 6.8 --. Column 10, line 46, "Kaiser NCO-120" should read -- Kaiser NCO-20 --.

Signed and sealed this 9th day of June 1970.



Attest:

*Edward A. Schuyler Jr.*

Attesting Officer

EXHIBIT

1

*William E. Schuyler Jr.*

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents

**3,409,579**  
**FOUNDRY BINDER COMPOSITION COMPRISING  
 BENZYLIC ETHER RESIN, POLYISOCYANATE,  
 AND TERTIARY AMINE**

Janis Robins, St. Paul, Minn., assignor to Ashland Oil & Refining Company, Ashland, Ky., a corporation of Kentucky

No Drawing. Continuation-in-part of application Ser. No. 569,106, Aug. 1, 1966. This application May 2, 1967, Ser. No. 635,382.

22 Claims. (Cl. 260—30.4)

**ABSTRACT OF THE DISCLOSURE**

A binder composition particularly suited for foundry aggregates is obtained by admixing a phenolic resin with a polyisocyanate and thereafter promoting the cross-linking of the mixture with a tertiary amine.

The present invention relates to binder compositions and to methods for curing such binder compositions. In another aspect, the present invention relates to binder compositions useful in the foundry art for making cores which harden at room temperature. In still another aspect, the present invention relates to combination of a foundry aggregate such as sand and a binder based on phenolic resins and polyisocyanates which, on being formed into a coherent mass with the aggregate, is capable of being cured at room temperature, preferably by the use of a gaseous curing agent. This application is a continuation-in-part of application Ser. No. 569,106 filed Aug. 1, 1966.

In the foundry art, cores for use in making metal castings are normally prepared from mixture of an aggregate material, such as sand, which has been combined with a binding amount of a polymerizable or curable binder. Frequently, minor amounts of other materials are also included in these mixtures, e.g. iron oxide, ground flax fibers, and the like. The binder permits such a foundry mix to be molded or shaped into the desired form and thereafter cured to form a self-supporting structure.

Typically, sand is used as the aggregate material. After the sand and binder have been mixed, the resulting foundry sand mix is rammed, blown, or otherwise introduced into a pattern, thereby assuming the shape defined by the adjacent surfaces of the pattern. Then by use of catalysts, e.g. chlorine and carbon dioxide, and/or the use of heat, the polymerizable binder is caused to polymerize, thereby converting the formed, uncured foundry sand mix into a hard, solid, cured state. This hardening can be accomplished in the original pattern, in a gassing chamber, or in the holding pattern. See U.S. Patents 3,145,438 and 3,121,168, which patents are illustrative of the prior art techniques.

Phenolic resins constitute one of the well-known classes of curable resin compositions used as binders in the foundry art. Both the novolac type of phenol-aldehyde resin and the "resole" or "A-stage" resins have been used in this type of application. Novolac resins are soluble, fusible resins in which the polymer chains have phenolic end-groups. They are traditionally prepared by condensing phenols with aldehydes using acid catalysts and employing a molar excess of phenol over aldehyde. Novolac resins can be cured to insoluble, infusible products by the addition of a source of formaldehyde such as hexamethylbenzene or paraform. Resole and resote resins, the latter being the more highly polymerized form of a resole resin, are generally prepared using an alkaline catalyst and excess aldehydes and result in polymers having a highly branched structure and therefore a high content

of alkyl end-groups. Since each alkyl group constitutes a potential cross-linking site, the resole and resote resins are readily converted to the cross-linked, infusible polymer by heating. The most commonly used monomers are phenol, i.e. hydroxybenzene, and formaldehyde for both the resole type and the novolac type of resin.

Although both the novolac resins and the resole resins have advantages and disadvantages characteristic of their different polymer structure in their application as foundry binders, both are subject to the deficiency of requiring heat in order to achieve the cured foundry form. Frequently, it is necessary to keep the green cores in the original molds or patterns during this heating period since many heat-curable binders do not impart sufficient green strength to cause green cores to retain their desired shapes without external support until such time as a final cure can be effected.

In an effort to prepare cores without the necessity of using heat, various prior attempts have been made to prepare binders which would be capable of curing at room temperature, i.e. at temperatures from about 45–120° F., more usually about 60–90° F. A variety of materials have been developed or suggested for use as binders, but these prior art compositions have suffered from one or more deficiencies.

Typical of the deficiencies exhibited by prior art binders alleged to cure at room temperature have been a lack of ability to rapidly impart green strength or stripping strength to cores, a lack of tensile strength, intolerably short bench life of foundry mixes, high toxicity, inability to combine well with all foundry aggregates, high sensitivity to moisture, contamination of the surface of castings, and the creation of pinholes in castings.

Although some of the heretofore developed binders capable of curing cores at room temperature, rapidly develop sufficient green strength to allow the removal of the core from the pattern, an additional period of up to 24 hours is frequently required in order to cause the cores to become cured and sufficiently strong to be used in the metal casting process.

It is therefore an object of the present invention to provide binder compositions and methods for curing such binder compositions.

It is an additional object of the present invention to provide binder compositions which are characterized by their ability to rapidly cure at room temperature when used in foundry mixes and which, in addition, exhibit one or more of the following properties:

- (a) moisture resistance,
- (b) high tensile strength,
- (c) adhesion to any aggregate commonly used in the foundry art,
- (d) the ability to impart an excellent level of moldability or plasticity to foundry sand mixes containing the novel binder composition,
- (e) a realistic bench life which generally is independent of the curing rate, and
- (f) the ability to form cores which result in excellent castings by reducing or eliminating the general problems of conventional air-drying binders, surface cracks, and surface contamination.

It is another object of this invention to provide foundry mixes based on the novel binder compositions of the present invention.

It is a further object of the present invention to provide a process for producing cores and other foundry shapes from foundry mixes incorporating the novel binder compositions of the present invention.

Still another object of the present invention is to provide foundry products containing the binder compositions of the present invention in cured form.

Other objects will become apparent from the following description and claims.

Broadly described, the binder compositions of the present invention are phenolic resins dissolved in non-aqueous systems which have been combined with sufficient polyisocyanate to cross-link the phenolic resins and are cured with tertiary amine.

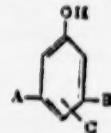
Although it has been known heretofore that isocyanates react with phenolic resins to result in cross-linked materials, heating has generally been employed to cause the isocyanate to react with the phenolic resin either through the phenolic hydroxyl group or through the methylol group in order to achieve the formation of cross-linking urethane bonds. According to the present invention, binder compositions are provided which cure at room temperature.

Phenolic resins have, as indicated above, been widely used as foundry binders. Regardless of whether a resole type of resin or a novolac type of resin is employed, the curing of such resins requires heating. The novolac resins require, in addition, a curing agent, preferably in the form of a formaldehyde source such as hexamethylene-tetramine. Considerable heating is required to cause the novolac resins to become cross-linked. The resole resins, on the other hand, although capable of rapid curing at elevated temperatures, are less suitable as binder compositions since they normally contain large quantities of water which can cause the formation of steam blisters, are thermally unstable and have a branched structure which causes them to be relatively insoluble and difficult to apply as a uniform coating on a sand particle. Such uniform coating is necessary in order to obtain even bonding of the aggregate and the formation of cores of acceptable tensile strength.

The use of polyisocyanates alone as a core binder does not result in cores which have sufficient tensile strength to make such cores useful for most industrial applications. Additionally, as the amount of polyisocyanate present in the foundry mix is increased, toxicity is generally believed to increase. Further, as the amount of polyisocyanate in a foundry mix is increased, there is an increasing tendency for castings to contain pinholes. It is generally believed that this pinholing is associated with the amount of nitrogen present in the binder. In the compositions of the present invention, however, the quantity of polyisocyanate is such as to avoid toxicity problems and pinholing problems.

The binder compositions of the present invention are generally made available as a two-package system comprising the resin component in one package and the hardener component in the other package, said resin component comprising an organic solvent solution of a non-aqueous phenolic resin, the said hardener component comprising a liquid polyisocyanate having at least two isocyanate groups per molecule. At the time of use, the contents of the two packages can be combined and then mixed with the sand aggregate or the packages can be sequentially admixed with sand aggregate. After a uniform distribution of the binder on the sand particles has been obtained, the resulting foundry mix is molded into the desired shape. The curing of the molded shape is accomplished by passing a tertiary amine through the molded shape. Employing the binder compositions of the present invention, curing can be accomplished in less than one minute. Since only very small amounts, i.e., catalytic concentrations, of the amine are necessary to accomplish rapid curing, one can, for example, volatilize small quantities of the tertiary amine into an inert gas stream such as nitrogen or air and pass such a stream through the molded shape. Any gas which does not itself enter into the reaction is considered an "inert gas" for the purposes of the present invention. In view of the porous nature of the shaped foundry mix, relatively low pressures are necessary to achieve the penetration of the molded shape by the gas.

Any phenolic resin which is substantially free of water and is soluble in an organic solvent can be employed. The term "phenolic resin" as employed herein is meant to define any polymeric condensation product obtained by the reaction of a phenol with an aldehyde. The phenols employed in the formation of the phenolic resin are generally all phenols which have heretofore been employed in the formation of phenolic resins and which are not substituted at either the two ortho-positions or at one ortho- and the para-position, such unsubstituted positions being necessary for the polymerization reaction. Any one, all, or none of the remaining carbon atoms of the phenol ring can be substituted. The nature of the substituent can vary widely and it is only necessary that the substituent not interfere in the polymerization of the aldehyde with the phenol at the ortho-position. Substituted phenols employed in the formation of the phenolic resins include: alkyl-substituted phenols, aryl-substituted phenols, cyanalkyl-substituted phenols, alkenyl-substituted phenols, 10 alkoxy-substituted phenols, aryloxy-substituted phenols, and halogen-substituted phenols, the foregoing substituents containing from 1 to 26 and preferably from 1 to 6 carbon atoms. Specific examples of suitable phenols, aside from the preferred unsubstituted phenol, include: 20 m-cresol, p-cresol, 3,5-xylenol, 3,4-xylenol, 2,3,4-trimethyl phenol, 3-ethyl phenol, 3,5-diethyl phenol, p-butyl phenol, p-octyl phenol, 3,5-dicyclohexyl phenol, p-phenyl phenol, p-crotyl phenol, 3,5-dimethoxy phenol, 3,4,5-trimethoxy phenol, p-ethoxy phenol, p-butoxy phenol, 3-methyl-4-methoxy phenol, and p-phenoxy phenol. Such phenols can be described by the general formula:



wherein A, B, and C are hydrogen, hydrocarbon radicals, oxyhydrocarbon radicals, or halogen. The preferred phenols are those which are unsubstituted in the para-position as well as in the ortho-positions. The most preferred phenol is the unsubstituted phenol, i.e., hydroxybenzene.

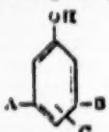
45 The aldehydes reacted with the phenol can include any of the aldehydes heretofore employed in the formation of phenolic resins such as formaldehyde, acetaldehyde, propionaldehyde, furfuraldehyde, and benzaldehyde. In general, the aldehydes employed have the formula R'CHO wherein R' is a hydrogen or a hydrocarbon radical of 1 to 8 carbon atoms. The most preferred aldehyde is formaldehyde.

The phenolic resins employed in the binder compositions can be either resole or A-stage resins or novolac resins. The resole or B-stage resins, which are a more highly polymerized form of resole resins, are generally unsuitable. The phenolic resin employed must be liquid or organic solvent-soluble. Solubility in organic solvent is desirable to achieve the uniform distribution of the binder on the aggregate. The substantial absence of water in the phenolic resin is desirable in view of the reactivity of the binder composition of the present invention with water. The term "non-aqueous" or substantially water-free as employed herein is meant to define a phenolic resin which contains less than 5% of water and preferably less than 1% of water based on the weight of the resin.

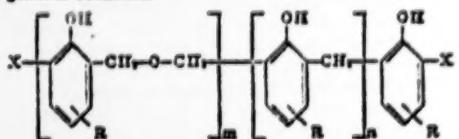
70 Although both the resole resins and the novolac resins can be employed in the binder compositions of the present invention, and, when admixed with polyisocyanates and a foundry aggregate and cured by use of tertiary amines to form cores of sufficient strength and other properties to be suitable in industrial applications, the novolac resins are preferred over the resole resins. Many resole resins, are difficultly soluble in organic solvents and thus do not permit a uniform coating of the aggregate particles.

Furthermore, novolac resins are generally prepared in aqueous media and even on dehydration contain 10 or more percent of water. Novolac resins generally have a more linear structure and thus are more readily soluble in organic solvents. Because of their higher molecular weight and absence of methylol groups, novolac resins can, furthermore, be more completely dehydrated. The preferred novolac resins are those in which the phenol is prevailingly polymerized through the two ortho positions. The preparation of novolac resins is known in the art and for that reason not specifically referred to herein.

Particularly preferred phenolic resins are condensation products of a phenol having the general formula:



wherein A, B, and C are hydrogen, hydrocarbon radicals, oxyhydrocarbon radicals, or halogen, with an aldehyde having the general formula R'CHO wherein R' is a hydrogen or a hydrocarbon radical of 1 to 8 carbon atoms, prepared in the liquid phase under substantially anhydrous conditions at temperatures below about 130° C. in the presence of catalytic concentrations of a metal ion dissolved in the reaction medium. The preparation and characterization of these resins is disclosed in greater detail in copending application Ser. No. 536,180 filed Mar. 14, 1966. In the preferred form, these resins have the general formula:



wherein R is a hydrogen or a phenolic substituent meta to the phenolic hydroxyl group, the sum of m and n is at least 2 and the ratio of m-to-n is at least 1, and X is an end-group from the group consisting of hydrogen and methylol, the molar ratio of said methylol-to-hydrogen end-groups being at least 1.

The phenolic resin component of the binder composition is, as indicated above, generally employed as a solution in an organic solvent. The nature and the effect of the solvent will be more specifically described below. The amount of solvent used should be sufficient to result in a binder composition permitting uniform coating thereof on the aggregate and uniform reaction of the mixture. The specific solvent concentrations for the phenolic resins will vary depending on the type of phenolic resins employed and its molecular weight. In general, the solvent concentration will be in the range of up to 30% by weight of the resin solution and preferably in the range of 20 to 30%. It is preferred to keep the viscosity of the first component at less than X-1 on the Gardner-Holt Scale.

The second component or package of the novel binder composition comprises an aliphatic, cycloaliphatic, or aromatic polyisocyanate having preferably from 2 to 5 isocyanate groups. If desired, mixtures of polyisocyanates can be employed. Less preferably, isocyanate prepolymers formed by reacting excess polyisocyanate with a polyhydrolic alcohol, e.g. a prepolymer of toluene diisocyanate and ethylene glycol, can be employed. Suitable polyisocyanates include the aliphatic polyisocyanates such as hexamethylene diisocyanate, cyclic polyisocyanates such as 4,4'-dicyclohexylmethane diisocyanate, and aromatic polyisocyanates such as 2,4'- and 2,6-toluene diisocyanate, diphenylmethane diisocyanate, and the dimethyl derivatives thereof. Further examples of suitable polyisocyanates are 1,3-naphthalene diisocyanate, triphenylmethane triiso-

cyanate, xylylene diisocyanate, and the methyl derivatives thereof, polymethylene-polyphenol isocyanates, chlorophenylene-2,4-diisocyanate, and the like. Although all polyisocyanates react with the phenolic resin to form a cross-linked polymer structure, the preferred polyisocyanates are aromatic polyisocyanates and particularly diphenylmethane diisocyanate, triphenylmethane triisocyanate, and mixtures thereof.

10 The polyisocyanate is employed in sufficient concentrations to cause the curing of the phenolic resin. In general, the polyisocyanate will be employed in a range of 10 to 500 weight percent of polyisocyanate based on the weight of the phenolic resin. Preferably, from 20 to 300 weight percent of polyisocyanate on the same basis is employed. The polyisocyanate is employed in liquid form. Liquid polyisocyanates can be employed in undiluted form. Solid or viscous polyisocyanates are employed in the form of organic solvent solutions, the solvent being present in a range of up to 80% by weight of the solution.

15 Although the solvent employed in combination with either the phenolic resin or the polyisocyanate or for both components does not enter to any significant degree into the reaction between the isocyanate and the phenolic resin in the presence of the curing agent, it can affect the reaction. Thus the difference in the polarity between the polyisocyanate and the phenolic resins restricts the choice of solvents in which both components are compatible. Such compatibility is necessary to achieve complete reaction 20 and curing of the binder compositions of the present invention. Polar solvents of either the protic or aprotic type are good solvents for the phenolic resin, but have limited compatibility with the polyisocyanates. Aromatic solvents, although compatible with the polyisocyanates, 25 are less compatible with the phenolic resins. It is therefore preferred to employ combinations of solvents and particularly combinations of aromatic and polar solvents. Suitable aromatic solvents are benzene, toluene, xylene, ethylbenzene, and mixtures thereof. Preferred aromatic solvents are mixed solvents that have an aromatic content of at least 90% and a boiling point range within 30 a range of 280° to 450° F. The polar solvents should not be extremely polar such as to become incompatible with the aromatic solvent. Suitable polar solvents are generally those which have been classified in the art as coupling solvents and include furfural, furfuryl alcohol, Cellosolve acetate, butyl Cellosolve, butyl Carbitol, diacetone alcohol, and "Texanol." Furfuryl alcohol is particularly preferred.

35 40 45 50 55 The binder components are combined and then admixed with sand or a similar foundry aggregate to form the foundry mix or the foundry mix can also be formed by sequentially admixing the components with the aggregate. Methods of distributing the binder on the aggregate particles are well-known to those skilled in the art. The foundry mix can, optionally, contain other ingredients such as iron oxide, ground flax fibers, wood cereals, pitch, refractory flours, and the like.

A valuable additive to the binder compositions of the 60 present invention in certain types of sand is a silane having the general formula:



65 where R' is a hydrocarbon radical and preferably an alkyl radical of 1 to 6 carbon atoms and R is an alkyl radical, an alkoxy-substituted alkyl radical, or an alkyloamino-substituted alkyl radical in which the alkyl groups 70 have from 1 to 6 carbon atoms. The aforesaid silane, when employed in concentrations of 0.1 to 2% based on the phenolic binder and hardener, improves the adhesion of the phenolic binder to the foundry aggregate particle.

The aggregate, e.g. sand, is usually the major constituent and the binder portion constitutes a relatively minor

amount, generally less than 100%, frequently within the range of 0.25 to about 5%, these figures being based on the weight of the aggregate. Although the sand employed is preferably dry sand, moisture of up to about 1 weight percent based on the weight of the sand can be tolerated. This is particularly true if the solvent employed is non-water-miscible or if an excess of the polyisocyanate necessary for curing is employed, since such excess polyisocyanate will react with the water.

The resulting foundry mix is then molded into the desired core or shape, whereupon it can be cured rapidly by contacting with the tertiary amine. The actual curing step can be accomplished by suspending a tertiary amine in an inert gas stream and passing the gas stream containing the tertiary amine, under sufficient pressure to penetrate the molded shape, through the mold until the resin has been cured. The binder compositions of the present invention require exceedingly short curing times to achieve acceptable tensile strengths, an attribute of extreme commercial importance. Optimum curing times are readily established experimentally. Since only catalytic concentrations of the tertiary amine are necessary to cause curing, a very dilute stream is generally sufficient to accomplish the curing. However, excess concentrations of the tertiary amine beyond that necessary to cause curing are not deleterious to the resulting cured product. Inert gas streams, e.g. air or nitrogen, containing from 0.01 to 5% by volume of tertiary amine can be employed. Normally gaseous tertiary amines can be passed through the mold as such or in dilute form. Suitable tertiary amines are gaseous tertiary amines such as trimethyl amine. However, normally liquid tertiary amines such as triethyl amine are equally suitable in volatile form or if suspended in a gaseous medium and then passed through the mold. Although ammonia, primary amines and secondary amines exhibit some activity in causing a room temperature reaction, they are considerably inferior to the tertiary amines. Functionally, substituted amines such as dimethyl ethanol amine are included within the scope of tertiary amines and can be employed as curing agents. Functional groups which do not interfere in the action of the tertiary amine are hydroxyl groups, alkoxy groups, amino and alkyl amino groups, ketoxyl groups, thio groups, and the like.

The binder compositions of the present invention have been principally defined and illustrated in terms of their use in the foundry art. Although the binder compositions are particularly suited for this application, the binders can also be employed in such applications as adhesives and coatings. In these applications, it is generally desirable to employ an amine such as pyridine or an amine oxide, which similarly catalyze the reaction between the phenolic resin and the polyisocyanate, although at a reduced rate which thereby allows their incorporation in the composition. The process in which the binders of the present invention are employed is believed to be novel and not necessarily limited to the described phenolic resins. Thus other hydroxyl group-containing resins such as copolymers of styrene and allyl alcohol result in foundry shapes containing a cured binder when employed in the process described in place of the phenolic resins. However, far superior properties are obtained when the described phenolic resins are employed.

The present invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated.

#### EXAMPLES 1 TO 20

Foundry sand mixes were prepared by admixing 20 parts of the phenolic resins further identified below, 20 parts of butyl acetate and the below-indicated amount of a mixture of di- and triphenylmethane, di- and triisocyanate commercially available as "Mondur MR" until uniform, and thereafter admixing the resulting binder 75

with 2,000 parts of silica sand until the binder was evenly distributed on the sand particles.

The resulting foundry sand mixes were then formed into standard Al-S tensile test samples, using the standard procedure. The resulting test samples were then cured by treatment with triethyl amine. In treating the samples with triethyl amine, an air stream was bubbled through the liquid triethyl amine and then passed through the test samples for a period of 60 seconds.

The cured samples were then stored in either a dry atmosphere or in an atmosphere of 100% relative humidity for a period of 2 hours before the tensile strength was measured.

The following phenolic resins were employed.

**Resin A.**—This resin was obtained by charging to a reflux system 720 g. of paraformaldehyde, 1014 g. of phenol, 15 g. of zinc naphthenate solution (8%), and 120 ml. of benzene. The system was heated to reflux (103° C. to 126° C.). After three hours, during which water and benzene were distilled off, 150 ml. of diethylene glycol dimethyl ether and 10 ml. of benzene were added. An additional 150 ml. of the ether were added after one further hour of refluxing. After five hours, 600 ml. of tetrahydrofuran were added to dilute the resin system. A total of 310 g. of water was distilled over. The resin and the solvent weighed 2320 g., and the resin was found to be a benzylic ether type of phenolic resin.

**Resin B.**—The procedure employed for Resin A was repeated except that 15 g. of lead naphthenate solution (24%) instead of the zinc naphthenate solution was employed. The reflux was continued for six hours at a temperature of 103° C. to 123° C. without the addition of the ether. A total of 298 ml. of water was distilled over. To the resin was added 100 ml. of benzene during the reflux, and 575 ml. of isopropanol at the end of the reflux. This resin was found to be a benzylic ether type of phenolic resin having a lower molecular weight than Resin A.

**Resin C.**—This resin was obtained by charging 292 g. of phenol, 63 g. of paraform, 2 g. of zinc naphthenate, and 100 g. of toluene. The reaction mixture was refluxed at 258° F. to 266° F. for a period of 6.5 hours and then heated to 380° F. The resulting resin was an o-o-phenol formaldehyde resin of the novolac type.

**Resin D.**—A commercially available (Syncro 1398C) acid-catalyzed phenol formaldehyde, novolac type resin.

**Resin E.**—A commercially available (Syncro 640) oil reactive novolac type resin obtained for p-t-butylphenol and formaldehyde.

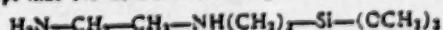
The results are illustrated in the following Table I.

TABLE I

Example	Resin	Isocyanate Content in parts	Exposure	Tensile Strength in p.s.i.
1.....	A	10	Dry	320
2.....	A	10	100% R.H.	30
3.....	A	10	Dry	320
4.....	A	10	100% R.H.	30
5.....	B	10	Dry	320
6.....	B	10	100% R.H.	30
7.....	B	10	Dry	320
8.....	B	10	100% R.H.	30
9.....	C	10	Dry	220
10.....	C	10	100% R.H.	10
11.....	C	10	Dry	10
12.....	D	10	100% R.H.	45
13.....	D	10	Dry	220
14.....	D	10	100% R.H.	35
15.....	D	10	Dry	140
16.....	D	10	100% R.H.	30
17.....	E	10	Dry	220
18.....	E	10	100% R.H.	10
19.....	E	10	Dry	20
20.....	E	10	100% R.H.	2

#### EXAMPLES 21 TO 29

The procedures of Examples 1 to 20 were repeated except that 1% of a silane having the formula



was added to the binder. The following results were obtained.

TABLE II

Example	Resin	Furyl-alcohol Content in parts	Exposure	Tensile Strength in p.s.i.
21	B	20	Dry	320
22	B	20	100% R.I.R.	430
23	B	10	Dry	320
24	B	10	100% R.I.R.	210
25	B	5	Dry	220
26	B	5	100% R.I.R.	300
27	D	10	100% R.I.R.	260
28	D	5	Dry	190
29	D	5	100% R.I.R.	180

## EXAMPLE 30

The procedure of Examples 1 to 20 was repeated using Resin B, 20 parts of the polyisocyanate, triethyl amine, and a gas cure time of 90 seconds. Tensile strength of

5,000 parts of sand in a Hobart mixer for a period of two minutes. To the resulting sand mixture was then added "Mondur MR" in the amounts indicated dissolved in the solvents shown in "Part B." The mixture was agitated for another two minutes and then blown into a "Redford" former at a pressure of 100 p.s.i. to form core test samples. As soon as the samples had been formed they were gassed by passing nitrogen at a pressure of about 81 p.s.i. through liquid triethyl amine and thereafter charging it to the core samples at a pressure of about 20 to 40 p.s.i. through the blow holes. The samples were gassed for 10 seconds and permitted to remain in the sample-forming machine for an additional one minute before removal.

15 Some of the samples, on gassing, were baked at 375° F. for 15 minutes, and of these some were exposed for two hours at 100% relative humidity at room temperature. Tensile strength measurements on all three types of samples were made, and are shown in the following Table III.

TABLE III

Example	Formulation (in parts)						Tensile Strength (in p.s.i.)		
	Part A			Part B			Gassed	Gassed and Baked	Gassed, Baked and Exposed
Resin	Furfuryl Alcohol	Furfural	Furfural	Aromatic Solvent <sup>1</sup>	Mondur MR				
17.5	7.5	-----	5	19.8	22.2	200	430	185	
17.5	7.5	-----	5	22.6	23	230	280	190	
17.5	7.5	-----	5	24.4	19.6	195	330	160	
17.5	7.5	-----	5	22	23	220	450	180	
17.5	7.5	-----	5	20	20	225	490	200	
17.5	3.3	4.3	-----	22	19	235	495	273	
17.5	7.5	-----	5	20	20	230	440	200	
15.5	6.5+	5	-----	22.5	23	235	440	250	

<sup>1</sup>Commercially available as "Solvesso-101."

Instead of "Mondur MR" another polyisocyanate, commercially available as "Kaiser NCO-120," was employed.

Test bar was 390 p.s.i. In a modification of this procedure, the test bar was cured by bubbling air through diethyl amine. The resulting test bar had a tensile strength of 20 p.s.i. In a third modification, the tensile bar was cured by blowing NH<sub>3</sub> through the bar. The resulting bar had a tensile strength of 60 p.s.i.

## EXAMPLE 31

Procedure of Examples 1 to 20 was repeated employing instead of the "Mondur MR" polyisocyanate, a styrene polyphenyl isocyanate commercially available as "Papi." The test bars were cured by treatment with diethyl amine, as described. Employing 20 parts of the polyisocyanate, a tensile strength on curing of 320 p.s.i. was obtained. Employing 10 parts of the polyisocyanate, a tensile strength of the gas cured test bar was 200 p.s.i.

## EXAMPLES 32 TO 39

A sealed kettle was charged 42.5 lbs. of phenol, 46.5 lbs. of formaldehyde, 0.95 lb. of a 24% solution of acetone in toluene, and 4 lbs. of toluene. The kettle was closed and heated to temperatures of 100° to 110° for a period of 3 hours. During this heating period the pressure was maintained at 2 to 4 p.s.i., and steam was admitted to the vessel as pressure increased. Some toluene was removed. After three hours, a vacuum was applied to the reaction mixture to remove all the toluene and 36.5 lbs. of furfuryl alcohol was added. 116 lbs. of resin obtained. The resin was of ether type.

It was diluted with solvents as indicated in "Part A," and admixed with

the procedure of Example 36 was repeated using the following commercially available polyisocyanates: "Baymidur K-33," "Suprasec DN," "PAPI," "Desmodur 44V," "Kaiser NCO-120," and "Carwinate 390 P." In all instances the tensile strengths of the samples were in the range of 230 to 350 p.s.i.

## EXAMPLE 40

Employing the procedure of Examples 31 to 39, different types of phenolic resins were evaluated. The following resins were employed.

55 **Resin A.**—A benzoic acid catalyzed novolac resin prepared with aqueous formaldehyde at a formaldehyde to phenol mole ratio of 0.8.

**Resin B.**—A zinc borate catalyzed novolac resin prepared with aqueous formaldehyde at a formaldehyde to phenol mole ratio of 0.8.

**Resin C.**—A low molecular weight acid catalyzed novolac resin in which the acid had been neutralized.

**Resin D.**—An acid catalyzed novolac resin in which the acid had been neutralized, prepared at low formaldehyde to phenol ratios.

**Resin E.**—Benzyllic ether resin prepared substantially as described in Examples 32 to 39.

The foundry aggregates were prepared as described in Examples 32 to 39, using the solvents indicated in Table IV. The aggregates were then permitted to stand for 10 and 60 minutes respectively before gassing. Those samples which were baked after gassing were directly blown and gassed without any delay subsequent to mixing. The samples were otherwise prepared as described in Examples 32 to 39, and their tensile strengths determined.

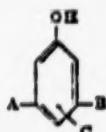
TABLE IV

Example	Resin	Formulation (parts/5,000 parts of sand)				Tensile Strength (p.s.i.)			
		Resin	Butyl Cellosolve	Furfural	Aromatic solvent <sup>1</sup>	Part B	Curing after 10 mins.	Curing after 60 mins.	Curing and Baking
41	A	19.5	16.5	-----	22	23	110	40	370
42		17	17	7	19	23	70	120	300
43	C	17.6	7.5	5	19.3	23	160	140	220
44	D	17.6	7.5	5	19.3	23	180	130	210
45	E	17.6	17.6	-----	22	23	120	200	180

<sup>1</sup>"Solvenso-100."<sup>2</sup>Furfuryl alcohol instead of Butyl Cellosolve.<sup>3</sup>Methylacetate instead of "Solvenso-100."

What is claimed is:

1. A binder composition comprising in admixture a resin component, a hardener component, and a curing agent, said resin component comprising an organic solvent solution of a non-aqueous phenolic resin which comprises a condensation product of a phenol having the general formula:



wherein A, B, and C are hydrogen, hydrocarbon radicals, oxyhydrocarbon radicals or halogen, with an aldehyde having the general formula R'CHO wherein R' is a hydrogen or a hydrocarbon radical of 1 to 8 carbon atoms; said hardener component comprising liquid polyisocyanate containing at least two isocyanate groups; and a curing agent comprising a tertiary amine.

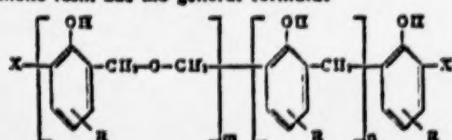
2. The binder composition of claim 1, wherein the aldehyde is formaldehyde.

3. The binder composition of claim 1, wherein the aldehyde is formaldehyde, and A and B are hydrogen, and C is a hydrocarbon radical.

4. The binder composition of claim 1, wherein the aldehyde is formaldehyde and A, B, and C are hydrogen.

5. The binder composition of claim 1, wherein the phenolic resin is a novolac resin.

6. The binder composition of claim 1, wherein the phenolic resin has the general formula:



wherein R is hydrogen or a phenolic substituent meta to the hydroxyl group of the phenol, m and n are numbers the sum of which is at least 2, and the ratio of m-to-n is at least 1, and X is a hydrogen or a methylol group, the molar ratio of said methylol group-to-hydrogen being at least 1.

7. The binder composition of claim 6, wherein R is hydrogen.

8. The binder composition of claim 1, wherein the polyisocyanate is an aromatic polyisocyanate.

9. The binder composition of claim 8, wherein the aromatic polyisocyanate is diphenylmethane diisocyanate.

10. The binder composition of claim 6, wherein the polyisocyanate is an aromatic polyisocyanate.

11. The binder composition of claim 1, wherein the solvent is a mixture of an aromatic solvent and a polar solvent.

12. The binder composition of claim 11, wherein the

13 polar solvent is furfural, furfuryl alcohol, Cellosolve acetate, butyl Cellosolve, butyl Carbitol, diacetone alcohol or mixtures thereof.

13. A foundry mix containing sand as the major constituent and a binding amount of up to 10% based on the weight of sand of the binder of claim 1.

14. A foundry mix containing sand as the major constituent and a binding amount of up to 10% based on the weight of sand of the binder of claim 6.

15. The process of preparing shaped foundry products

25 which comprises:

(a) forming a foundry mix by uniformly distributing on a foundry aggregate containing sand as the major constituent a binding amount of up to 10% based on the weight of the aggregate of a binder composition obtained by combining the phenolic resin component and hardener component of claim 1, said polyisocyanate being employed in a concentration of 10 to 500% by weight of the phenolic resin;

(b) shaping the foundry mix in a mold; and

(c) contacting the shaped foundry mix with a tertiary amine until the binder has cured.

16. The process of claim 15, wherein the tertiary amine is passed through the shaped foundry mix in gaseous form.

40 17. The process of claim 15, wherein the tertiary amine is gaseous at room temperature.

18. The process of claim 15, wherein the tertiary amine is suspended in an inert gas stream which is passed through the shaped foundry mix.

19. The process of claim 15, wherein the resin component of the binder is the phenolic resin of claim 6.

20. The process of claim 19, wherein the polyisocyanate is an aromatic polyisocyanate.

21. The process of claim 17, wherein the tertiary amine is trimethyl amine or triethyl amine.

22. The process of claim 15, wherein the foundry mix is prepared by admixing the foundry aggregate with the phenolic resin component and thereafter admixing the resulting mixture with the hardener component.

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MORRIS LIEBMAN, Primary Examiner.

70 R. S. BARON, Assistant Examiner.

# United States Patent

Robins

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(45) July 11, 1972

## [54] RESIN COMPOSITIONS

[72] Inventor: Janis Robins, St. Paul, Minn.  
[73] Assignee: Ashland Oil Inc., Houston, Tex.  
[22] Filed: Jan. 26, 1971  
[21] Appl. No. 109,944

### Related U.S. Application Data

[61] Continuation-in-part of Ser. No. 72,113, Sept. 14, 1970, and a continuation-in-part of Ser. No. 723,873, April 23, 1968, abandoned, and a continuation-in-part of Ser. No. 369,106, Aug. 1, 1966, Pat. No. 3,429,818, and a continuation-in-part of Ser. No. 536,180, March 14, 1966, Pat. No. 3,485,792.

[51] U.S. CL..... 260/38, 260/59, 260/DIG. 40  
Int. CL..... C08g 5/06  
[52] Field of Search..... 260/38, 59, DIG. 40; 164/43

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Primary Examiner—Lewis F. Jacobs  
Assistant Examiner—S. M. Person  
Attorney—Walter H. Schneider

EXHIBIT

2

## [57] ABSTRACT

Novel resin compositions comprising mixture of organic solvent soluble phenolic resin containing benzyl ether linkage and/or methylol end group with polyisocyanate and catalytic concentrations of a base. The resin compositions are capable of curing at room temperature and are useful as coating and binder compositions.

17 Claims, No Drawings

# I RESIN COMPOSITIONS RELATED APPLICATIONS

This application is a continuation in part of the following prior applications: Ser. No. 72,113 filed Sept. 14, 1970; Ser. No. 723,873 filed Apr. 24, 1968, now abandoned; Ser. No. 569,106, filed Aug. 1, 1966, now U.S. Pat. No. 3,429,648 issued Feb. 25, 1969; and Ser. No. 536,180, filed Mar. 14, 1966 now U.S. Pat. No. 3,485,797 issued Dec. 23, 1969.

The present invention relates to resin compositions which are mixtures of certain phenolic resins and polyisocyanates. In another aspect the present invention relates to curable binder compositions which are useful in bonding particulate solids such as aggregates. In still another aspect, the present invention relates to combinations of a foundry aggregate, such as sand, and a binder based on certain phenolic resins and polyisocyanates which, on being formed into a coherent mass with the aggregate, is capable of being cured at room temperature.

10 Foundry cores are prepared from mixtures of aggregate material, such as sand, which has been combined with a binding amount of a polymerizable or curable binder. Frequently, lesser amounts of other materials are also included in these cores, e.g., iron oxide, ground flax fibers, and the like. The binder permits such a foundry mix to be molded or shaped into the desired form and thereafter cured to form a self-supporting structure.

15 Typically, sand is used as the aggregate material. After the sand and binder have been mixed, the resulting foundry sand is rammed, blown, or otherwise introduced into a pattern, thereby assuming the shape defined by the adjacent surfaces of the pattern. Then by use of catalysts, e.g., chlorine and carbon dioxide, and/or the use of heat, the polymerizable binder is caused to polymerize, thereby converting the formed, unshaped foundry sand mix into a hard, solid, cured state. This curing can be accomplished in the original pattern, in a curing chamber, or in the holding pattern. See U.S. Pat. Nos. 3,04,816 and 3,121,266, which patents are illustrative of the art techniques.

20 Phenolic resins constitute one of the well known classes of resin compositions used as binders in the foundry art. The novolac type of phenol-aldehyde resin and the "A-stage" resin have been used in this type of application. Novolac resins are soluble, fusible resins in which the polymer chains have phenolic end groups. They are traditionally prepared by condensing phenols with aldehydes using acid catalysts and employing a molar excess of phenol over aldehyde. Novolac resins can be cured to insoluble, infusible polymers by the addition of a source of formaldehyde such as paraformaldehyde or paraformaldehyde. Resole and novolac resins being the more highly polymerized form of a novolac resin, are generally prepared using an alkaline catalyst, formaldehyde and result in polymers having a highly cross-linked structure and therefore a high concentration of aldehyde groups. Since each aldehyde group constitutes a cross-linking site, the resole and novolac resins are suited to the cross-linked, infusible polymer. The most commonly used monomers are phenol, i.e., novolac and formaldehyde for both the resole type and the novolac type of resin. Although both the novolac and resole resins have advantages and disadvantages, and their different polymer structure, in their use as foundry binders, both have been subject to the requirement of heat in order to achieve the cure. Frequently, it is necessary to keep the foundry molds or patterns during this heating cycle.

25 Many heat-curable binders do not impart sufficient strength to cause green cores to retain their external support mold such time as a pattern is removed.

30 Other novolac or resole resins to cure at room temperature are similarly exhibited in some cases in novolac resins find utility. Such heat-inert include

in particular molding compositions in which the phenolic resin is admixed with inert organic and inorganic fillers, coating compositions and adhesive compositions.

35 It is therefore an object of the present invention to provide novel resin compositions, capable of curing without heating.

It is another object to provide novel resin compositions based on mixtures of certain types of phenolic resins and isocyanates.

40 It is a further object to provide binder compositions based on certain types of phenolic resins, in admixture with polyisocyanates and base catalysts.

It is yet another object to provide binder compositions particularly suitable for the bonding of particulate solids.

45 Still a further object of the present invention is to provide novel foundry products based on the novel resin compositions of the present invention.

It is still another object of the present invention to provide a process for producing cores and other foundry shapes from foundry mixes incorporating the novel resin compositions of the present invention.

50 Yet another object of the present invention is to provide cold-curable phenolic resin compositions which combine long bench life with fast curing times and superior bond strength properties.

Other objects will become apparent from the following description and claims.

Broadly described, the binder compositions of the present invention comprise organic solvent phenolic resins containing hydroxyl ether structure and/or methylol end group in non-aqueous systems which have been combined with sufficient polyisocyanate to cross-link the phenolic resin and which contain as the curing catalyst a base having a  $pK_a$  value in the range of about 7 to about 11, as determined in a known manner, as described below.

55 The determination of  $pK_a$  values of organic compounds may be made in various conventional manners depending upon the nature of the particular organic compound. The  $pK_a$  values of compounds useful as catalysts in this invention may be determined according to methods described by D. D. Perrin in *Dissociation Constants of Organic Bases in Aqueous Solution* (Hilbertworths, London 1963).

Although it has been known heretofore that isocyanates react with phenolic resins to result in cross-linked materials, heating has generally been found to be necessary to result in cross-linked materials having acceptable properties. This has been particularly true where such mixtures of phenolic resins and polyisocyanates are employed in combination with a particulate solid such as a foundry aggregate. In the absence of heating the shaped aggregates have low tensile strength and are also deficient in other mechanical properties. These deficiencies are overcome by the compositions of the present invention which combine the use of a particular type of phenolic resin and a particular base catalyst.

In addition to the catalytic activity of causing curing at room temperature the base catalysts of the present invention add a highly surprising and desirable property to the resin compositions. Most conventional resin compositions combine long bench life with long cure times or short cure times with short bench lives. The resin compositions of the present invention for reasons not clearly understood combine long bench life with short cure times which result in superior mechanical properties in the cured product.

60 The resin compositions of the present invention are generally made available as a two package system comprising the phenolic resin component in one package and the polyisocyanate hardener component in the other package, both components being in liquid form and therefore generally comprising organic solvent solutions. In general the catalyst is incorporated into the resin component although such is not essential. At the time of use, the contents of the two packages are combined and used in the intended application. In foundry applications it is particularly desirable to facilitate one component with the foundry aggregate to retain sand and thereafter

add the second component and mix it with the resulting mixture. After a uniform distribution of the binder on such as the sand particles in the foundry application has been obtained, the resulting foundry mix is molded into the desired shape. The shaped product can be immediately removed from the mold and on standing at room temperature will form a cured product. The time required for curing will vary with the nature of the base catalyst and more particularly with pH<sub>4</sub> value of the catalyst. Although the resin compositions of the present invention are particularly designed to achieve curing at room temperature, it is to be understood that these resin compositions can also be cured by baking at elevated temperatures.

The benzyl ether resins which comprise one species of the phenolic resins employed in the present invention are characterized by containing a unit having the formula:

(II)



wherein A, B, and C are hydrogen, hydrocarbon radicals, oxyhydrocarbon radicals or halogen, the R's are individually H or hydrocarbon radical of one to eight carbon atoms and which have average degrees of polymerization, as measured by the number of repeating aromatic rings, of generally 1 to 100 and preferably 4 to 10. Although higher molecular weight resins are operable in the curing reactions above described, such resins are difficult to handle from the standpoint of viscosity in requiring excessive amounts of solvents to bring the viscosity of the resin component to a level normally desired in coating and binder applications.

The described benzyl ether resins are condensation polymers of a phenol having the general formula:

(III)



wherein A, B and C are hydrogen, hydrocarbon radicals, oxyhydrocarbon radicals or halogen, with an aldehyde having the general formula R'CHO wherein R' is a hydrogen or a hydrocarbon radical of one to eight carbon atoms, prepared in the liquid phase in the substantial absence of water at temperatures below about 130°C in the presence of catalytic concentrations of a metal ion dissolved in the reaction medium. Molar ratio of aldehyde to phenol can generally be varied 3:1 to 1:1, although some resin is also formed outside these ratios. The preparation and characterization of these are disclosed in greater detail in copending application No. 416,180, filed Mar. 14, 1966 now U.S. Pat. No. 3,797 issued Dec. 23, 1973. In the preferred form, these have the general formula:



It is a hydrogen or a phenolic substituent meta to the hydroxyl group, the sum of m and n is at least 2, X is a group consisting of hydrogen and one or more methylol groups, at least 2, and wherein m is at least 1 and the sum of m and the methylol groups is at least 2.

The most preferred benzyl ether resins employed in the resin compositions of the present invention are those in which R is hydrogen.

- 5 The phenols employed in the formation of the benzyl ether resins are generally all phenols which have heretofore been employed in the formation of phenolic resins generally and which are not substituted at either of the carbon atoms ortho to the hydroxyl group. Any one, all, or none of the remaining carbon atoms of the phenol ring can be substituted. 10 The nature of the substituent can vary widely and it is only necessary that the substituent not interfere in the polymerization of the aldehyde with the phenol at the ortho-position. Substituted phenols employed in the formation of the phenolic resins include alkyl substituted phenols, aryl-substituted phenols, cycloalkyl-substituted phenols, alkenyl-substituted phenols, alkoxy-substituted phenols, aryloxy-substituted phenols, and halogen-substituted phenols, the foregoing substituent containing from one to 26 and preferably from one to six carbon atoms. Specific examples of suitable phenols, aside from the preferred unsubstituted phenol, include: m-cresol, p-cresol, 3,5-xylenol, 3,4-xylenol, 2,3,4-trimethyl phenol, 3-ethyl phenol, 3,5-diethyl phenol, p-outyl phenol, 3,5-dibutyl phenol, p-amyl phenol, p-cyclohexyl phenol, p-octyl phenol, 3,5-dicyclohexyl phenol, p-phenyl phenol, p-tert-butyl phenol, 3,5-dimethoxy phenol, 3,4,5-trimethoxy phenol, p-methoxy phenol, p-butoxy phenol, 3-methyl-4-methoxy phenol, and p-phenoxy phenol.

The aldehydes reacted with the phenol can include any of the aldehydes heretofore employed in the formation of phenolic resins such as formaldehyde, acetaldehyde, propionaldehyde, furfuraldehyde, and benzaldehyde. In general, the aldehydes employed have the formula R'CHO wherein R' is a hydrogen or a hydrocarbon radical of one to eight carbon atoms. The most preferred aldehyde is formaldehyde.

The methylol-terminated phenolic resins useful in the present invention are resole resins which are organic solvent soluble. The organic solvent soluble resole resins are a well established class of resins the preparation of which is known. However, since the resole resins having a high proportion of ortho/ortho methylene linkages are generally the organic solvent soluble resole resins, the majority of the resole resins useful in this invention are prepared from alkyl-substituted phenols wherein the para position is substituted. On the other hand, organic solvent soluble resole resins may also be prepared from phenols unsubstituted in the ortho and para positions by first preparing an ortho/ortho novolac and then reacting the novolac with further formaldehyde under milder conditions to produce a methylol-terminated resin which is an organic solvent soluble resole resin unsubstituted at the para positions. As an illustration of this procedure, a mixture of phenol and formaldehyde wherein the molar ratio of phenol-formaldehyde is greater than 1:1 may be condensed in the presence of an ortho/ortho directing catalyst, such as sodium hydroxide, under alkaline pH, e.g. between 5 and 6, and at a temperature in the neighborhood of 110°C. When essentially no free formaldehyde remains, the excess phenol is removed by vacuum distillation and the resin cooled to the melting point of 40°C or 50°C. Addition of formaldehyde is then added and the subsequent exothermic reaction controlled to keep the temperature below about 95°C. This mixture is then rapidly cooled before the resin becomes insoluble, which results in a methyl-terminated organic solvent soluble resole resin having essentially no para substitution and the same is true in this invention. The disclosures of British Pat. Nos. 773,511 and 773,547 are particularly pertinent to the above resole resins prepared from phenol unsubstituted in the meta and para positions.

The phenolic resin component is generally employed as a solution in an organic solvent although it is also feasible to employ the low molecular weight liquid resins without dilution. The durability and effect of solvents and substances used is described in greater detail. The optimum solvent concentra-

tions for the phenolic resins will vary depending on the type of resin employed and its molecular weight. In general, the solvent concentration will be in the range of up to 50% by weight of the resin solution and preferably in the range of 20 to 50 percent. It is preferred to keep the viscosity of the resin component at less than No. 4 on the Gardner-Holt Scale.

The catalyst employed in the compositions of the present invention is a base having a  $pK_a$  value in the range of about 7 to about 11. The  $pK_a$  value is the negative log (arithm) of the dissociation constant of the base and is a well known measure of the basicity of a basic material. The higher this number is, the weaker the base. The bases falling within this range are generally organic compounds containing one or more nitrogen atoms. Preferred materials are heterocyclic compounds containing at least one nitrogen atom in the ring structure. Specific examples of bases which have  $pK_a$  values within the necessary range include alkyl pyridines wherein the alkyl group has from one to four carbon atoms; quinuclidine, aryl pyridines such as phenyl pyridine, pyridine acridine, 2-methoxypyridine, pyridazine, 3-chloro pyridine quinoline, N-methyl imidazole, 4,4-dipyridine, phenyl propyl pyridine, 1-methylbenzimidazole, and 1,4-thiazine.

In view of the varying catalytic activity and varying catalytic effect desired, catalyst concentrations will vary widely. In general the lower the  $pK_a$  value is, the shorter will be the bench life of the composition and the faster, more complete will be the cure. Solvents and any acidity present in added ingredients such as sand may affect the catalytic activity. In general, however, catalyst concentrations will range from 0.01 to 10 percent by weight of the phenolic resin.

The second component or package of the novel binder composition comprises an aliphatic, cycloaliphatic, or aromatic polyisocyanate having preferably from two to five isocyanate groups. If desired, mixtures of polyisocyanates can be employed. Less preferably, isocyanate prepolymers formed by reacting excess polyisocyanate with a polyhydroxy alcohol, e.g., a prepolymer of toluene diisocyanate and ethylene glycol, can be employed. Suitable polyisocyanates include the aliphatic polyisocyanates such as hexamethylene diisocyanate, bicyclic polyisocyanates such as 1,4'diethylhexylmethane diisocyanate, and aromatic polyisocyanates such as 1,3- and 2,6-toluene diisocyanate, diphenylmethyl diisocyanate, and the dimethyl derivatives thereof. Further examples of suitable polyisocyanates are 1,5-naphthalene diisocyanate, triphenylmethane triisocyanate, vinylene diisocyanate, and the methyl derivatives thereof, polymethylene polyphenol isocyanates, chlorophenylene-2,4-diisocyanate, and the like. Although all polyisocyanates react with the described phenolic resin to form a cross-linked polymer structure, the preferred polyisocyanates are aromatic polyisocyanates and particularly diphenylmethane diisocyanate, triphenylmethane triisocyanate, complex commercially available compositions containing polymeric isocyanates sold under such trademarks as "PAPI," "Mondur MR" and "St. O-120," and mixtures thereof.

The polyisocyanate is employed in sufficient concentrations to cause the curing of the phenolic resin and other active hydrogen-containing materials when present. This refers to materials with hydrogen atoms which display acidity according to the well-known Zetewall method as described by Lichten in JACS, 49, 1181 (1927). Thus tertiary amine, phenyl-formaldehyde resins of the Novolac and/or resole types having an average of two or more active hydrogen atoms per molecule may be employed. For information on Novolac and resole the disclosures of U.S. Pat. Nos. 3,242,107 and 3,301,171 and British Pat. No. 757,392 are herein incorporated by reference to the extent pertinent. When present the total weight of such other active hydrogen-containing materials should not exceed three times the weight of the phenolic resin and should preferably be less than that of the phenolic resin. In general, the polyisocyanate will be employed in a range of 10 to 50 weight percent of polyisocyanate based on the weight of the phenolic resin comprising

Preferably, from 20 to 40 weight percent of polyisocyanate on the same basis is employed. The polyisocyanate is employed in liquid form. Liquid polyisocyanates can be employed in undiluted form. Solid or viscous polyisocyanates are employed in the form of organic solvent solutions, the solvent being present in a range of up to 80 percent by weight of the solution.

Although the solvent employed in combination with either the phenolic resin or the polyisocyanate or for both components does not enter, to any significant degree into the reaction between the isocyanate and the phenolic resin, it can affect the reaction. Thus the difference in the polarity between the polyisocyanate and the benzyl ether resins restricts the choice of solvents in which both components are compatible. Such compatibility is necessary to achieve complete reaction and curing of the resin compositions of the present invention. Additionally, the solvent, by reducing the viscosity of the binder, aids in the uniform distribution of the resin composition on a substrate or a particulate solid. Polar solvents of either the protic or aprotic type are good solvents for the phenolic resin, but have limited compatibility with the polyisocyanates. Aromatic solvents, although compatible with the polyisocyanates, are less compatible with the phenolic resins. It is therefore preferred to employ combinations of solvents and particularly combinations of aromatic and polar solvents. Suitable aromatic solvents are benzene, toluene, xylene, ethylbenzene, m-pentene, and mixture thereof. Preferred aromatic solvents are mixed solvents that have an aromatic content of at least 90 percent and a boiling point range of 280° to 450° F. The polar solvents should not be extremely polar such as to become incompatible with the aromatic solvent. Suitable slightly polar solvents which are compatible with aromatic solvents include, in particular, ester and ether solvents. Suitable more polar but less easily solvents are generally those which have been classified in the art as coupling solvents and include furfural, furfuryl alcohol, cellosolve acetate, butyl cellosolve, butyl carbitol, diacetone alcohol, and "Texanil."

On combining the two components of the resin composition of the present invention, the resulting mixture is capable of cross linking at room temperature to form a coating or a binder for particulate solids. In the foundry art, the binder or its components are admixed with sand or a similar foundry aggregate to form the foundry mix. Methods of distributing the binder or its components on the aggregate particles are well known to those skilled in the art. The foundry mix can, optionally, contain other ingredients such as iron oxide, ground flux fibers, wood creosote, pitch, refractory flours, and the like.

A valuable additive to the binder compositions of the present invention is a silane having the general formula:



wherein R' is a hydrocarbon radical and preferably an alkyl radical of one to six carbon atoms and R'' is an alkyl radical, in alkyl-substituted alkyl radical or an alkylamino-substituted alkyl radical in which the alkyl groups have from one to six carbon atoms. The above silane, when employed in concentrations of 0.1 and 2 percent based on the phenolic binder and hardener, improves the adhesion of the phenolic binder to the foundry aggregate particle.

Illustrative of the active radicals which may be bonded by the resin compositions of this invention are solid or hollow pellets of carbon, aluminum, steel, and other metals and glass, as well as other non-combustible glass and ceramic materials. The active radicals bonding on the major constituent and the binder portion of the composition and every minor constituent of the composition should be distributed uniformly within the composition. 25 weight percent of the active radicals based on the weight of the composition will result in a curing agent having a greater than 90% conversion rate.

weight percent based on the weight of the aggregate can be tolerated. This is particularly true if the solvent employed is not water miscible or if an excess of the polyisocyanate necessary for curing is employed, since such polyisocyanate will react with the water, thereby reducing the poisoning effect of the water on the metal ion.

Of particular interest is the binding of foundry aggregate, e.g., sand, with the resin compositions of this invention. In general the resin composition can be mixed with the foundry aggregate or each of the phenolic resin and polyisocyanate components mixed with the foundry aggregate in series or mixed with separate portions of foundry aggregate and the separate portions of foundry aggregate mixed together. The catalyst is usually added to either the phenolic resin or isocyanate component prior to mixing with the aggregate. The resulting foundry mix is then molded into the desired core or shape, whereupon it can be cured either slowly or rapidly on standing at room temperature.

The resin compositions of this invention have various other uses, such as protective or decorative coating and foundry core pastes. In these uses the resin compositions are used alone or with other materials, such as additional solvents, fillers or pigments.

The present invention is further illustrated by the following examples in which, unless otherwise indicated, all parts are by weight and all percentages are weight percentages.

#### EXAMPLE 1

Into a sealed kettle was charged 62.5 lbs. of phenol, 46.5 lbs. of paraformaldehyde, 0.95 lb. of a 24 percent solution of lead naphthenate in toluene and 4 lbs. of toluene. The vessel was sealed and heated to temperatures of 100° to 125° C for a period of 3 hours. During this heating period, the pressure was maintained at 2 to 4 psi, and steam release from the vessel as pressure increased. Some toluene distilled out with the steam. A total of 24 lbs. of water was removed. After 3 hours, a vacuum was pulled on the reaction mixture to remove all the toluene originally added. The resin was of the benzene ether type as defined in formula III.

To parts of the resin solution was then added 1 percent 4,4'-dipyridine. Fifty parts of the resin solution were admixed with 5,000 parts of Wedron silica sand until uniformly distributed. A liquid polyisocyanate hardener solution comprising 60 parts of a commercially available polyisocyanate ("Mondur MR," a mixture of di- and triphenylmethane, di- and triisocyanate, and 20 parts of aromatic solvent (Hi-Sol 96C described hereinafter) was prepared. Fifty parts of the liquid polyisocyanate was added to the sand and resin mixture and uniformly distributed.

The resulting foundry mix was formed into standard AFS tensile test samples using the standard procedure. The tensile strength of the test bars were 20 psi after 2 hours, 110 psi after 4 hours, 200 psi after 24 hours and 220 psi after 16 hours at 125° F.

#### EXAMPLE 2

Using solely the resin of Example 1, the following resin and hardener solutions were made up:

##### Resin Solution

52% Resin of Example 1  
22% Cellulose Acetate  
25% Aromatic Solvent  
1% 1,4-Di-4-pyridyl propane

##### Hardener Solution

80% Polyisocyanate  
20% Aromatic Solvent

The aromatic solvent employed in the formulation of the solutions was commercially available "Bennigan Hi-Sol 96C" having a boiling point range of 174° to 164° F with a mixed azeotropic point of 57° F. The polyisocyanate was commercially available "Mondur MR." Fifty parts of each of the resin solution and the hardener were combined and admixed with 100 parts of Wedron silica sand. The resulting foundry mix was

then formed into standard AFS tensile test samples using the standard procedure.

The test samples were tested for compressive strength to establish at what time such samples could be removed from the mold. In general a 10 psi compressive strength is considered a minimum before removal of the sand form. The following results were obtained.

	Compressive Strength in psi
After 7 minutes	0.2
After 9 minutes	0.6
After 13 minutes	61
After 16 minutes	89
After 18 minutes	99

Thus it will be seen that curing in the mold could be reduced to about 13 minutes.

The test bars had tensile strengths of 40 psi after 10 minutes, 65 psi after 1 hour, 160 psi after 2 hours, 240 psi after 4 hours and 320 psi after about 16 hours at 125° F.

#### EXAMPLE 3

Resin and Hardener solutions were made up according to Example 2 except that 1 percent of 4-phenyl-propyl pyridine was employed instead of the dipyrindyl propane and a foundry mix was prepared from these solutions as described in Example 2. The resulting foundry mix was found to have a bench life of 13 minutes and could be removed from the mold with sufficient strength for free curing within 10.5 minutes. The tensile strength of the test bars after 4 hours was 220 psi and after 16 hours at 125° F 270 psi.

#### EXAMPLE 4-10

Resin solutions containing 52 parts of the resin of Example 1, 22 parts of cellulose acetate, 25 parts of the aromatic solvent used in Example 2 and the indicated amounts (Table I) of 4-dipyrindyl propane were made up.

Foundry mixes were made using 5,000 parts of Wedron silica sand, 50 parts of the resin solution and 50 parts of the hardener solution of Example 2. The bench life and the mold time for these mixes was established. Tensile bars made according to AFS procedures were air cured and their tensile strength measured. The following results were obtained.

TABLE I

Example	% Catalyst (min)	Bench Life (min)	Mold Time Cure (min)	Tensile Strength (psi)	
				Time 1 (hr)	2-4 Over-night
55	4	0.7	7	10	120 190 240 350
	5	0.6	8	11.5	80 140 210 290
	6	0.5	6.5	12	80 140 220 320
	7	0.4	13	17	65 130 230 370
	8	0.3	15	21	55 125 215 350
	9	0.2	14	34	10 30 140 150
60	10	0.1	100	--	5 10 20 280

#### EXAMPLE 11

Into a sealed kettle was charged 75 lbs phenol, 38 lbs paraformaldehyde (91 percent), 0.1 lb. lead naphthenate and 0.05 lb. lead oxide. The vessel was sealed and heated to a temperature of 240°-255° F. Water began to distill over. After 1 hour, 12 lb. water was removed, and the percent free formaldehyde was less than 1 percent. Full vacuum was then applied for 30 minutes and the reactor was cooled to 20° F and drained.

According to gel permeation chromatography, 7.09%, the average molecular weight was 1,610 to 2,010 and the formaldehyde to phenol mole ratio was 1.4. Calculated from inherent viscosity, 1.6, intrinsic viscosity of the resins defined in formulas I, II and III.

A resin solution was prepared containing 52 percent by weight of the above resin, 22 percent cellulose acetate, 25 percent of the aromatic solvent of Example 2 and 0.2 percent of 1,1-di-4-pyridyl propane. Fifty parts of the above resin solution and 50 parts of the hardener solution of Example 2 were consecutively admixed with 5,000 parts of Wedron silica sand. The resulting founders mix was then formed into standard AFS tensile test samples using the standard procedure.

The test samples were tested for compressive strength to establish at what time such samples could be removed from the mold. In general, a 10 psi compressive strength is necessary before removal. The following results were obtained:

	Compressive Strength (psi)
After 10 minutes	0.5
After 25 minutes	1.4
After 50 minutes	60

### EXAMPLE 12

50 parts of phenol, 58 parts of formalin (37 percent, 2 parts NaOH (50 percent aqueous) are charged to a kettle and heated to about 60°C. After the reaction exotherm takes off, cooling is applied to maintain temperature at about 77°C for about 2 hours as the reaction continues. Then 6 parts of bis(olefene sulfonic acid solution (50 percent aqueous) is introduced, following which vacuum is continuously applied to hydrate the reaction mass until the temperature rises to 88° whereupon the resultant resole resin is cooled and drained from the kettle.

A resin solution was prepared containing 59 percent by weight of the above resole resin, 50 percent cyclohexanone and 1 percent phenylpropyl pyridine. Fifty parts of the above solution and 50 parts of a solution containing 65 percent by weight of commercially available "NC O-120" polyisocyanate and 15 percent by weight of commercially available "HPSOL", an aromatic solvent having a boiling range of 120° to 140° and a mixed aminic point of 58°F, were consecutively admixed with 5,000 parts of Wedron silica sand. The resulting founders mix was then formed into standard AFS tensile test bars using standard procedure. The bars were air cured and the tensile strengths measured. The following results were obtained:

Initial life was 7 minutes.

Hold time was 8.5 minutes.

Time (hours)	Tensile Strength (psi)
1	160
2	200
4	240
5	170
Initial	

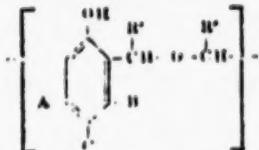
A resin composition comprising an admixture of a phenolic component, a hardener component, and a curing catalyst. The phenolic component is (a) an organic solvent soluble benzyl ether resin which contains benzyl ether group and (b) comprises a condensation polymer of a phenol having the general formula:



In A, B and C are hydrogen, hydrocarbon radicals, or halogen radicals or halogen, combined with an alkyl having the general formula R'C(R)C, wherein R' is one or a hydrocarbon radical of five to eight carbon atoms in the presence of catalytic concentrations of a metal catalyst a methylated terpenoid phenolic resin which contains

a resinous resin which is organic solvent soluble; said hardener component is a liquid polyisocyanate containing at least two isocyanate groups, and is present in an amount equal to 10 to 500 weight percent based on the weight of the resin and said curing agent is a base having a pH value in the range of about 7 to about 11 and is present in an amount equal to 0.01 to 10.0 weight percent based on the weight of the resin.

2. The resin composition of claim 1, wherein the resin component is a benzyl ether resin which contains a unit of the formula:



wherein A, B and C are hydrogen, hydrocarbon radicals, or hydrocarbon radicals, or halogen, and wherein R' is a hydrogen or a hydrocarbon radical of one to eight carbon atoms.

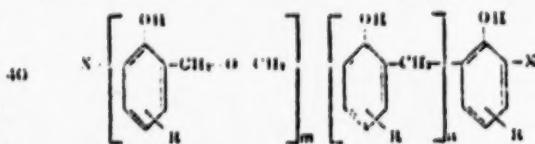
3. The resin composition of claim 2, wherein the aldehyde is formaldehyde.

4. The resin composition of claim 2, wherein the aldehyde is formaldehyde, and A and B are hydrogen, and C is a hydrocarbon radical.

5. The resin composition of claim 2, wherein the aldehyde is formaldehyde and A, B and C are hydrogen.

6. The resin composition of claim 1, wherein the resin component is a benzyl ether resin which is obtained by polymerizing the phenol and the aldehyde in the liquid phase in the substantial absence of water at temperatures below 130° C.

7. The resin composition of claim 1, wherein the resin component is a benzyl ether resin which it is the general formula:



wherein R is hydrogen or a phenolic substituent meta to the hydroxyl group of the phenol, m and n are numbers the sum of which is at least 2, X is an end-group from the group consisting of hydrogen and methylol, and wherein m is at least 1, and the sum of m and the number of methylol end-groups is at least 2.

8. The resin composition of claim 7, wherein R is hydroxyl.

9. The resin composition of claim 1, wherein the polyisocyanate is an aromatic polyisocyanate.

10. The resin composition of claim 9, wherein the aromatic polyisocyanate is diphenylmethane diisocyanate.

11. The resin composition of claim 7, wherein the polyisocyanate is an aromatic polyisocyanate.

12. The resin composition of claim 1, wherein the base is a nitrogen compound.

13. The resin composition of claim 1, wherein the base is a heterocyclic nitrogen compound.

14. The resin composition of claim 1, wherein the base is pyridine or a derivative of pyridine.

15. The resin composition of claim 1, wherein the base is a 4-alkyl pyridine wherein the alkyl group has from one to four carbon atoms, isopropylidene, an N,N-pyridine, acetyl, 2-methoxy pyridine, 4,4-dipropylene or phenylpropyl pyridine.

16. A founders mix containing sand as the major constituent and a bonding amount of up to 100 percent based on the weight of sand of the resin composition of claim 1.

17. A founders mix containing sand as the major constituent and a bonding amount of up to 100 percent based on the weight of sand of the resin composition of claim 7.

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7.4 It is understood and agreed by the parties hereto that the technical assistance provided for in this Agreement shall be applicable only to Technical Information and the use thereof in the manufacture of Binder Systems, including the quality control and quality assurance associated with the manufacture of commercially acceptable Binder Systems and that the technical assistance provided for by this Agreement shall not extend to any aspect of field testing or end use of Binder Systems in the foundries.

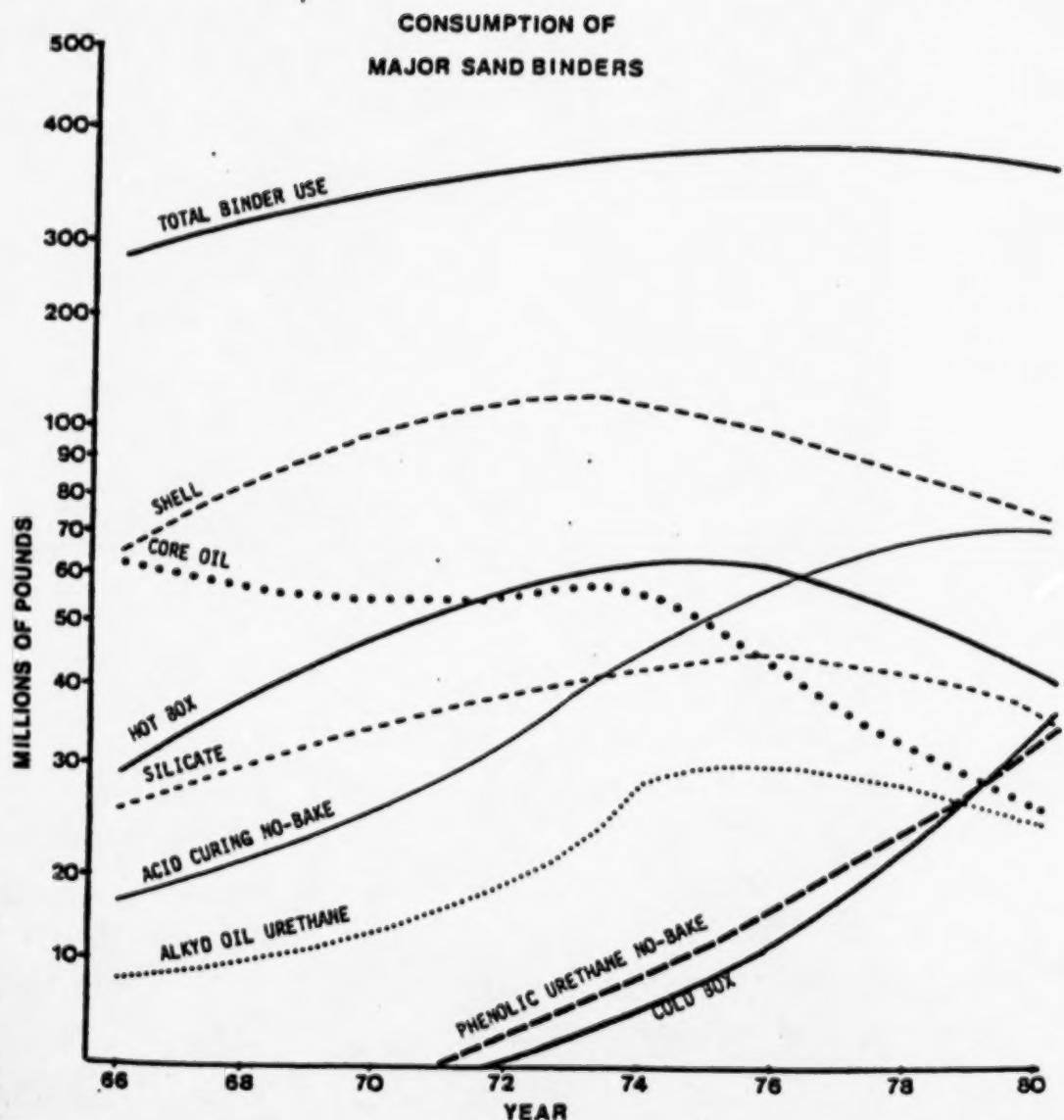
#### ARTICLE VIII

##### Effective Date, Duration and Termination

8.1 This Agreement shall become effective as of the date appearing on the first page hereof (referred to as "Effective Date") and unless sooner terminated as provided herein, this Agreement shall continue until July 11, 1989, provided, however, that upon termination or expiration of this Agreement the secrecy obligation of Article VI shall continue in force for an additional period of ten (10) years therefrom.

8.2 If any payment under this Agreement shall be in arrears and remain unpaid for a period of three months next following the end of any six-month period; or if either party is in breach or violation of any of the other duties, covenants or undertakings of this Agreement and has not remedied same within three months after notice thereof is given to the party in breach or violation by the other party; or if LICENSEE shall go into liquidation whether voluntary or compulsory or suffer the appointment of a receiver of a majority of its assets, then this Agreement may be terminated

1760  
160



## ASHLAND DOMESTIC FOUNDRY CUSTOMERS

ISOCURE® AND PEP SET®

## I. Direct Sales:

<u>Foundry Employment</u>	<u>Number of Foundries</u>	<u>Number of Customers Pep Set</u>	<u>Number of Customers Isocure</u>	<u>Total Isocure &amp; Pep Set Customers</u>
2500 and over	14	2	12	14
1000 to 2499	35	11	15	26
500 to 999	70	14	21	35
250 to 499	228	51	64	115
Under 250	4321	191	78	269

## II. Distributor Sales:

Not Categorized		161	104	265
TOTALS	4668	430	294	724